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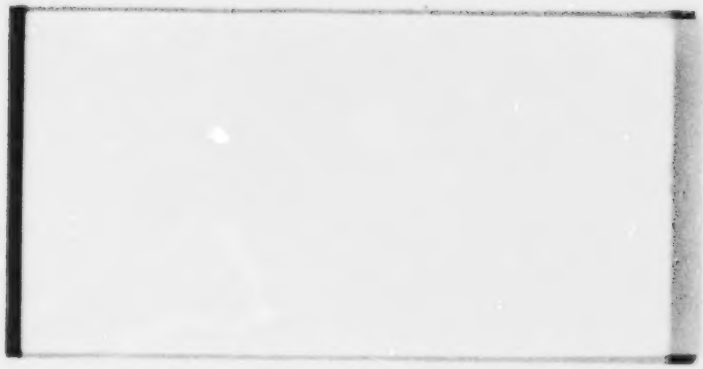

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ELECTROLYTIC HYDROGEN PRODUCTION
EXISTING AND EMERGING TECHNOLOGIES

Report No 85-210-K

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ABSTRACT

Electrolytic hydrogen generation technologies have been evaluated in order to identify the improvements necessary to increase the cost competitiveness of electrolytic hydrogen and to assess their suitability for other non-utilization applications in Ontario Hydro. Alkaline and SPE electrolyzer technologies require improvement in energy efficiency and cost reduction, respectively. High temperature water vapour electrolysis, which is still in the early stages of development, offers the most economic and efficient method for hydrogen generation, as part of the energy required for splitting water can be derived from external sources. The vapour phase electrolyzer based on proton conducting ceramic electrolytes, is being developed at Queens and McMaster Universities, and should be of interest to Ontario Hydro. This electrolyzer shows the promise of generating hydrogen efficiently, while utilizing part of the waste heat from CANDU Nuclear Stations. A number of other non-utilization applications are possible.

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740631-553-082	836.7	October 2, 1985	85-210-K

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EXECUTIVE SUMMARY

ELECTROLYTIC HYDROGEN PRODUCTION
EXISTING AND EMERGING TECHNOLOGIES

R.K. Kalia

Increased use of hydrogen, in a full fledged Hydrogen Energy Economy or a Mixed Hydrogen Energy Economy, would affect Ontario Hydro by creating a new load for electrolytic hydrogen generation. It would also offer the possibility of load levelling and bulk energy storage. The penetration of nuclear (electrolytic) hydrogen into the Canadian market will depend on the cost of electrolytic hydrogen compared to other competing technologies. There is a very wide divergence of opinion, in the literature, with respect to the future cost of electrolytic hydrogen in all stages of its production-consumption cycle. One major reason for these differences is the assumption made about the status of different technologies.

The objective of this report is to evaluate existing and emerging electrolytic hydrogen generation technologies and identify the developments that could improve their cost competitiveness. The suitability of different technologies for other non-utilization applications, such as: electrolytic decomposition of tritiated water, hydrogen isotope separation and tritium concentrators, is also discussed.

Alkaline electrolyzer technologies are well established and require low capital costs. Most commercial alkaline electrolyzers have low energy efficiencies (<80%, based upon higher heating value of hydrogen). Intensive efforts are being made to improve these efficiency levels; however, the extent to which improvements are possible seems limited.

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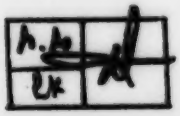
The SPE electrolyzer technology is the most efficient of the commercially available technologies but its high cost, mainly attributable to the Nafion membrane and precious metal electrocatalysts, hinders its widespread use. No breakthroughs that could substantially lower the cost, are expected in the near future.

High temperature water vapour electrolysis promises to be the most economic and efficient method, as part of the energy required for electrochemical splitting of water can be derived from external heat sources such as: solar heat, nuclear waste heat or recovered process heat. Electrolyzers based on ceramic oxide ion electrolytes have been investigated the most but are still in the laboratory stages of development. Since these electrolyzers operate at 600-1000°C they require high temperature waste heat; however, high temperature operation poses immense material problems.

A new Canadian technology, based on proton conducting ceramic electrolytes, is being developed at Queens and McMaster Universities, and shows the promise of eliminating the above problems of high temperature operation. This new technology is aimed at electrolyzing water vapours at 100-350°C so that the material problems are manageable, and the waste heat from a CANDU system can be utilized. Still in the early stages of development, this technology offers the promise for application in electrolysis of tritiated water. Slightly modified versions of electrolyzer may be used as tritium (or hydrogen) concentrator, tritium getter and fuel cell.

Other exotic electrochemical technologies for hydrogen generation include photoelectrolysis and electrolysis using anodic depolarizers. In these cases, part of the energy required for splitting water molecules is supplied in the form of light or chemical energy. Large scale production of hydrogen using photoelectrochemical cells appears unlikely since the scaling up of such cells is difficult. Small scale applications (eg, decomposition of tritiated water using photodiodes or photocatalytic powders) are possible.

Electrochemical coal gasification (the use of coal slurry as anodic depolarizer in water electrolysis) is an interesting concept but considerable improvements must be accomplished before acceptable current densities (1000-5000 A/m^2) can be obtained. The use of sulfur dioxide (from stacks) as an anodic depolarizer can alleviate acid rain problems but considerable fundamental and process engineering studies are necessary to evaluate the feasibility of the process.



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To Mr. F.J. Kee
Director of Research

ELECTROLYTIC HYDROGEN PRODUCTION
EXISTING AND EMERGING TECHNOLOGIES

R.K. Kalia

1.0 INTRODUCTION

There is growing awareness that the reserves of traditional fossil fuels are rapidly being exhausted. Exactly when the impact of the scarce supplies of fossil fuels will be felt is the subject of controversy; however, there seems to be no doubt that it will occur.

Nuclear resources are often considered to be the potential alternative to meeting our energy demands in the future. While it is true that most devices which consume energy can be modified to operate on electricity, there appear to be certain areas that are not served by electricity. Transportation, which accounts for about 50% of Canada's petroleum consumption/1/, is one of these areas. Proponents of the Hydrogen Energy Economy argue that in the absence of fossil fuels, hydrogen produced from water using nuclear energy can serve as a single energy carrier to meet all our energy needs for stationary as well as mobile applications. The opposing group argues that in the presence of substantial (and increasing) reserves of natural gas, coal, tar sand and oil shale, it is unlikely that a full fledged hydrogen economy will be realized - at least in the near term (~50 years).

Hydrogen already plays an important role in the chemical industry, such as in ammonia production. It seems extremely likely that the role of hydrogen will be much more significant in the future. Most of the hydrogen used in Canada (and in fact, the world) is produced by reforming fossil fuels such as natural gas. As the remaining fossil resources become more expensive and heavier, it is prudent to add more and more hydrogen from non-fossil resources, thereby increasing the carbon utilization efficiency. Thus, hydrogen may soon prove to be very important in the transportation sector, but not necessarily as a combustible fuel. Tar sand processing and synthetic fuel production are examples of the indirect use of hydrogen in an energy sector.

In Canada, nuclear (electrolytic) hydrogen can play a major role in a hydrogen/mixed hydrogen energy economy. The penetration of nuclear hydrogen into the Canadian market will ultimately depend on the cost of electrolytic hydrogen compared to other competing technologies. There is a wide divergence of opinion in the literature, with respect to the future costs of electrolytic hydrogen in all stages of its production consumption cycle. These differences stem from the varying assumptions made about the cost of electricity, capital investment, financing methods, interest rates, rate of return on investment, overhead expenses and the status of technology. Assuming the same cost of electricity, the cost of electrolytic hydrogen is mainly dependent on the capital costs of the electrolyzer plant and its energy efficiency. Current Solid Polymer Electrolyte (SPE) electrolyzer technology offers the highest energy efficiency of all the commercially available electrolyzers but its widespread use is being hindered by the extremely high capital costs. Conventional alkaline electrolyzer technologies, on the other hand, have low capital costs but also low energy efficiencies.

This report takes an in-depth look into available and emerging technologies in order to identify needed improvements which could result in improving the cost competitiveness of electrolytic hydrogen.

In Ontario Hydro, electrolyzer technologies may find other applications, not necessarily related to electricity utilization. Electric utilities including Ontario Hydro, use hydrogen as a coolant for electrical generating equipment, and rather than purchasing hydrogen for this requirement, it could be produced in-house. Other applications include: electrolytic decomposition of tritiated water, hydrogen isotope separation and tritium concentrators (for the recovery of gaseous tritium from contaminated air). This report attempts to identify the technologies that might find application in these areas.

2.0 ELECTROLYTIC PRODUCTION OF HYDROGEN

Electrolysis of water is the simplest and cleanest method for making hydrogen from water. Electrolysis cells essentially operate with no moving parts and offer the physical separation of hydrogen and oxygen. In principle, cells can be operated at high pressure with no efficiency penalty, so that electrolysis also provides the most energy conservative means of producing high pressure hydrogen gas. Cell size is small and many cells can be cascaded and paralleled. In commercial installations, the plant output could be tailored virtually to any level without sacrificing important economies of scale. The oxygen by-product could be used in all its current uses as well as in many

new ones such as oxygen-enhanced sewage treatment, solid waste disposal and oxygenation of natural bodies of water.

2.1 Fundamentals of Water Electrolysis

When a direct current is passed through water between two electrodes, water decomposes according to Equation (1).

$$H_2O \rightarrow \frac{1}{2} O_2 + H_2 \qquad (1)$$

The component reactions describing the overall reaction (1) are the discharge of H_2 at the cathode and O_2 at the anode. Cathodic and anodic reactions in an alkaline electrolyzer are:

At cathode

$$4H_2O + 4e \rightarrow 2H_2 + 4OH^- \qquad (2)$$

At anode

$$2OH^- \rightarrow O_2 + 2H^+ + 4e^- \qquad (3)$$

The following reactions take place in an acid electrolyte.

At cathode

$$4H_3O^+ + 4\bar{e} \rightarrow 4H_2O + 2H_2 \qquad (4)$$

At anode

$$6H_2O \rightarrow 4H_3O^+ + 4e^- + O_2 \qquad (5)$$

It requires two Faradays of electricity to produce 1 g mole of H_2 at 0°C and 760 torr (or 6.95 cm^3 of H_2/A min or 0.49 m^3/1000 A h, at 20°C and atmospheric pressure) assuming the current efficiency to be 100%.

An electrolytic hydrogen generator consists of the following basic components:

An Electrolyte: This is an aqueous solution made conductive by mixing a salt or compound with water. An electrolyte must have the following characteristics:

(a) exhibit high ionic conductivity;
(b) not be chemically decomposed by voltages as large as that applied to the cell (so that only water is decomposed);
(c) not be volatile enough to be removed with the evolved gases; and
(d) have a strong resistance to pH changes.

Salts are themselves decomposed at voltages likely to be encountered in a water electrolyzer. Acid electrolytes present severe corrosion problems and are usually avoided as electrolytes. Most commercial electrolyzers use an alkaline electrolyte. A KOH solution possesses maximum conductivity at about 30% concentration, which is the concentration usually selected.

One notable exception to the use of alkaline electrolytes is the use of solid polymeric ion exchange materials. Alkaline ion-exchange resins are sensitive to chemical degradation at elevated temperatures whereas acid ion-exchange resins are stable up to 160°C. The most successful work with ion exchange electrolytes has, therefore, been carried out using a polymerized fluorinated polystyrene sulfonic acid.

Electrodes: The electrodes should have the following characteristics:

(a) be electronic conductors;
(b) have suitable catalytic surface for the discharge of hydrogen or hydroxyl ions;
(c) provide adequate sites for nucleation of gas bubbles; and
(d) provide a reasonable means for the detachment of gas bubbles so that they may separate themselves from the electrolyte at the operating voltage of the cell.

The form of the electrodes varies considerably from one cell design to another. Large surface areas are obtained by the use of sintered structures, perforated plates and flat plates with electrochemically roughened faces.

In alkaline cells, nickel is the most commonly used catalytic surface. Rather than making electrodes out of solid nickel, nickel plated mild steel is often used. The application of precious metal catalysts such as platinum allows the electrode processes to proceed more rapidly than on nickel, but the extra cost of the precious metal is not usually considered justifiable.

In the case of a polymeric acid electrolyte, electrodes must be made of materials with more chemical resistance than nickel or steel. Pt, Rh and Ir are usually considered necessary as catalysts.

Separator: Required between the two electrodes in order to prevent short-circuiting of the electrodes and mixing of the hydrogen and oxygen gases inside the cell. To provide these functions properly, the separator must consist of a porous diaphragm or matrix through which the electrolyte solution can pass, affording an ionic conducting path from one side of the cell to the other. These pores must remain full of liquid so that the gas cannot penetrate them. Additionally, the separator material must not be corroded by the electrolyte in the presence of hydrogen or oxygen and it must remain structurally stable for the entire operating life of the cell so that the pores do not collapse.

To keep the ionic resistance of the cell as low as possible, the separator is usually made in the form of a thin sheet, the thickness of which is determined by the mechanical strength and gas crossover limitations. In the case of alkaline cells, asbestos in the form of woven cloth or matted fibres is commonly used as the separator material. Some experimental materials such as potassium titanate are also being developed.

In the case of polymeric acid ion-exchange resin, this material acts as its own separator; and no additional material is needed.

2.2 Thermodynamics of Water Electrolysis

The thermodynamic decomposition voltage corresponding to the Gibbs free energy change of reaction (1) of 56.69 k cal/g mole (at 25°C and one atmosphere pressure) is 1.229 V. Since the enthalpy (ΔH) of reaction (1) is 68.32 k cal/g mole (at 25°C and one atmosphere pressure), this reaction is endothermic. This difference between free energy change and enthalpy change arises from the entropy change in the overall process and must be balanced by supplying heat to the system. Because ΔG is smaller than ΔH, it is theoretically possible, and indeed also practical at very minute net currents, to achieve an energy efficiency of 100%/2/, 121% ($\Delta H/\Delta G$) being the theoretical maximum. Thus, if electrolysis is carried out at a cell potential between the reversible potential and the thermoneutral potential (corresponding to $\Delta H/nF$) (Figure 1), the electrolyzer requires heat as well as electricity input to maintain isothermal operation. At cell potentials above the thermoneutral potential, heat must be removed from the electrolyzer. In practice, all electrolyzers operate above the thermoneutral potential so that external cooling must always be provided. The energy efficiency is thus, always less than 100%.

Efficiency of an Electrolyzer

It is customary to define the electrical-energy efficiency of an electrolyzer as η, where

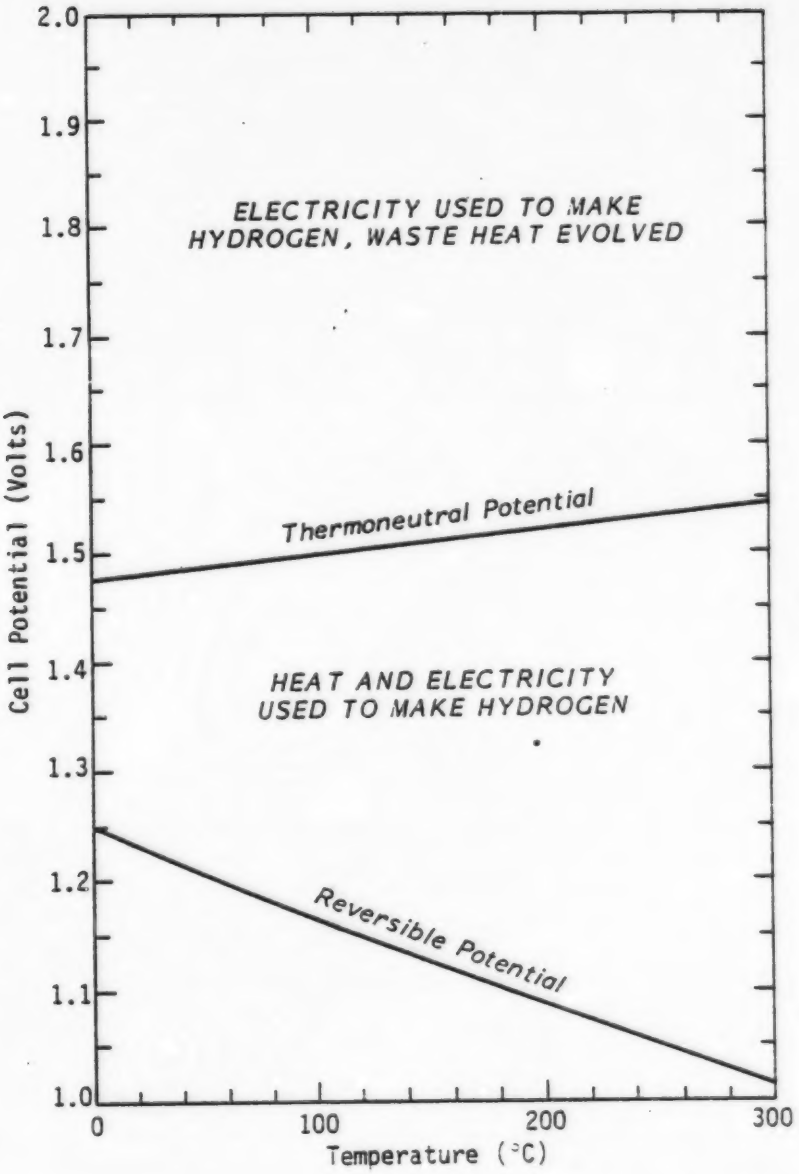


FIGURE 1

THE CELL POTENTIAL FOR WATER ELECTROLYSIS AS A FUNCTION OF TEMPERATURE/2/. THE THERMONEUTRAL POTENTIAL IS BASED ON THE HIGHER HEATING VALUE (HHV) OF HYDROGEN WHILE THE REVERSIBLE POTENTIAL IS BASED ON THE FREE ENERGY CHANGE FOR THE REACTION(1).

$$\eta = \frac{V_{HHV}}{V_{obs}} \qquad (6)$$

This definition has become widely accepted in accordance with efficiency measurements for other chemical fuel production processes although it would never be possible to recover the full higher heating value of hydrogen in an energy application.

V_{HHV} is defined as

$$V_{HHV} = [H(H_2)_T + H(O_2)_T - H(H_2O)25°C]/nF \qquad (7)$$

where H refers to the enthalpy of the species noted in the parenthesis. Thus, a water electrolysis cell operating at 2.5 V, and for example at 25°C, has an energy efficiency of (1.48/2.5) x 100 = 59.2%.

The operating cell voltages and energy efficiencies for present and projected electrolyzer technologies are shown in Table I. Power requirements per kg of hydrogen are also shown.

2.3 Components of Cell Voltage

The power consumption for operating water electrolysis cells is directly proportional to the cell voltage and inversely proportional to the current efficiency. Since the current efficiency for all electrolyzers is close to 100%, the parameter of importance in evaluating various designs of water electrolysis cells is the magnitude of the cell voltage, which is composed of the following components:

$$E = E_{rev} + \eta_a + \eta_c + \eta_r + \eta_{hw}$$

Where E_{rev} refers to the thermodynamic decomposition voltage η_a to the anodic overpotential, η_c to the cathodic overpotential, η_r to the ohmic drop across the electrolyte and η_{hw} to the ohmic drop through the hardware. Figure 2/2/ shows the contributions of different cell voltage components in a unipolar alkaline electrolyzer.

Different components of cell voltage can be calculated as shown in the following sections. Possible ways of reducing these voltage components are also discussed.

TABLE I/3/

PRESENT AND FUTURE COMPARISON OF
OVERALL EFFICIENCIES OF VARIOUS ELECTROLYZER CELLS

MANUFACTURER	PRESENTLY AVAILABLE POTENTIAL			2-5 YEAR PROJECTION POTENTIAL			FUTURE (ULTIMATE) POTENTIAL		
	kWh/kg	V	%*	kWh/kg	V	%	kWh/kg	V	%
Teledyne	70.5	2.1	75	42-48	1.6-1.8	82-92	15	1.24	118
General Electric	48.5	2.0	74	40-48	1.5-1.8	82-98	15	1.24	118
Stuart	54	2.04	72	50.2	1.9	77**	--	--	--
Life Systems	45	1.7	87	39.9	1.5	98	15	1.24	118
De Nora	--	1.85	80	--	1.8	82	--	--	--

* % efficiency defined by $\frac{\text{higher heating value of hydrogen produced}}{\text{electrical energy consumed}} \times 100$.

** Recent discussions with Dr. G. Belanger of IREQ indicate that efficiencies of the order of 85% have been demonstrated with an advanced version of the Stuart cell. Pilot tests have recently been completed at IREQ.

2.3.1 Thermodynamic Decomposition Voltage

Effect of Temperature: The energy efficiency of an electrolyzer can be improved by operating the cells at higher temperatures, since the theoretical minimum of electrical energy (ie, the thermodynamic decomposition voltage, E_{rev}) is lower at high temperatures, while the temperature dependence of the higher-heating - value voltage and thermoneutral voltages is small (Figure 1). Furthermore, the kinetics of electrode reactions and ion transport are accelerated at higher temperatures.

The temperature dependence of E_{rev} and E_{HHV} may be calculated/4/ from Equations (8) and (9) with results presented in

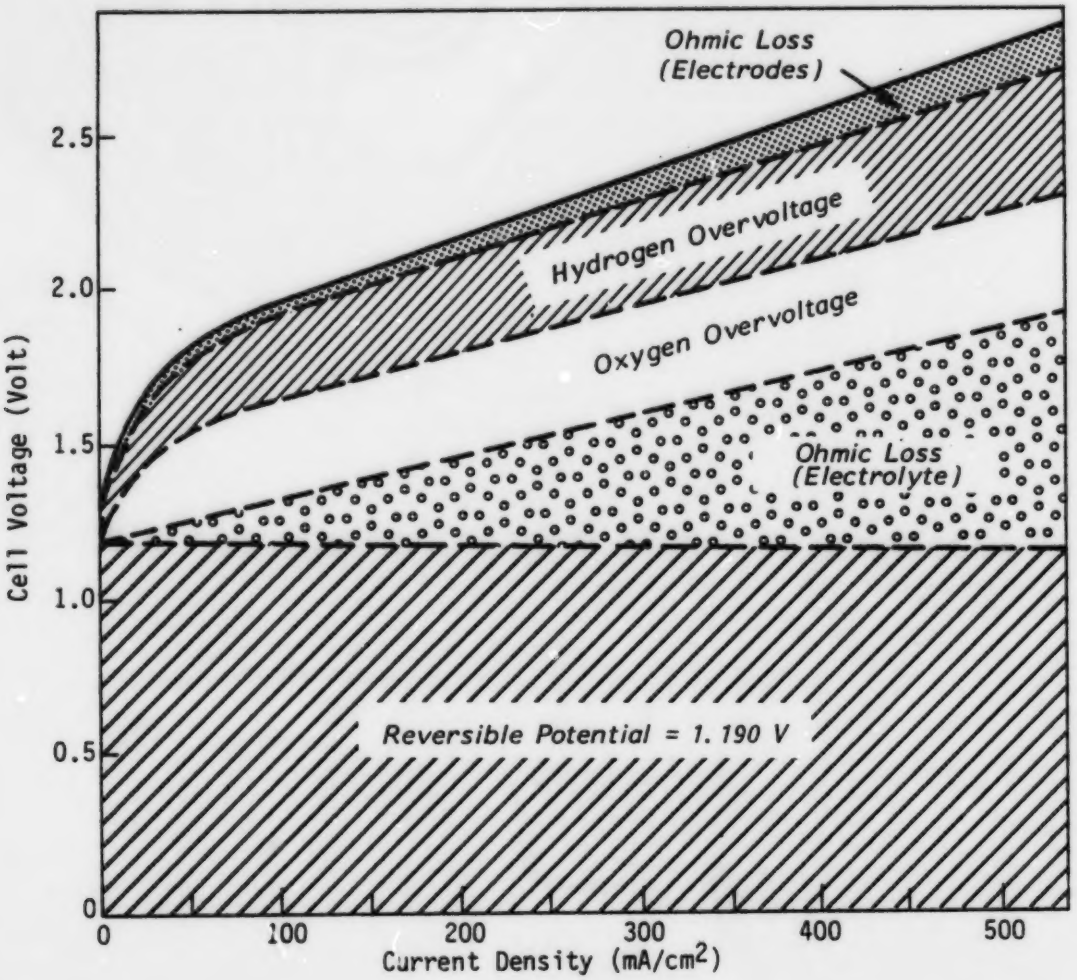


FIGURE 2

THE SINGLE CELL VOLTAGE FOR A UNIPOLAR ALKALINE WATER ELECTROLYSER OPERATING AT 70°C /2/.

Figure 1. E_{rev} varies from 1.229 V at 25°C to 1.040 V at 264°C but E_{HHV} shows a relatively small temperature coefficient, increasing from 1.481 V at 25°C to 1.536 at 264°C:

$$E_{rev} = 1.5184 - 1.5421 \times 10^{-3}T + 9.523 \times 10^{-5}T \ln T + 9.84 \times 10^{-8}T^2 \quad (8)$$

$$E_{HHV} = 1.415 + 2.169 \times 10^{-4}T + 1.52 \times 10^{-8}T^2 \quad (9)$$

T in Equations (8) and (9) is expressed in degrees Kelvin.

Equation (9) can be derived/4/ by substituting Equation (10) (describing ΔH variations with temperature) into Equation (11), which takes into account the energy requirements involved in heating the feed water from temperature T_f to T.

$$\frac{\Delta H_T}{nF} = 1.5475 - 3.2312 \times 10^{-4}T + 4.820 \times 10^{-7}T^2 - 4.82 \times 10^{-10}T^3 \quad (10)$$

$$V_{HHV} = \frac{\Delta H_T}{nF} + \frac{1}{nF} \int_{T_f}^{T} \overline{C_p}\ (H_2O)dT \quad (11)$$

where $C_{p(H_2O)}$ refers to the heat capacity of water.

Effect of Pressure

Raising the pressure of operation of a water electrolyzer results in a theoretical increase in the decomposition voltage of 43 mV for every ten fold increase in pressure as given by Equation (12)/3/,

$$E_p = E_1 + 0.0435 \log p \quad (12)$$

where p is the pressure of operation (in atmospheres) and E_p and E_1 are the decomposition potentials at operating pressures of p and 1 atmospheres, respectively.

The energy required to provide this additional voltage is exactly equal to the potential energy contained in the high pressure hydrogen. In practice, electrolyzer cells operate slightly closer to the ideal at higher pressures than they do at atmospheric pressure, that is, the efficiency losses are less at higher pressures. This is so because of a variety of reasons, including the fact that gas bubbles evolved are smaller and provide less hindrance to the passage of ionic current across the cell.

At pressures of up to 27 atmospheres, the saving in energy due to increased efficiency is greater than the extra energy that has to be expended to overcome the theoretical voltage/3/. Thus, pressurized operation of electrolyzers is an extremely efficient way of generating pressurized hydrogen, and, up to moderate pressure increases, pressure can be developed at an apparent pumping efficiency of greater than 100%.

2.3.2 Ohmic Overpotential

Ohmic drop between anode and cathode is a substantial contribution to the cell voltage although smaller than other overvoltage losses. It is composed of two components:

$$\eta_\Omega = \eta_{\Omega\ \text{electrolyte}} + \eta_{\Omega\text{separator}}$$

where $\eta_{\Omega\text{electrolyte}}$ is the potential drop across the gas - electrolyte mixture and $\eta_{\Omega\text{separator}}$ is the ohmic drop across the separator. While the former is minimized by cell design, the major ohmic losses arise across the separator. In order to minimize the $\eta_{\Omega\text{separator}}$ it is desired that the pore size and voidage should be large while the thickness should be small. But these requirements are opposite to the ones imposed by the basic necessity of the separator, ie, separation of product gases.

Ohmic losses (as well as other overvoltages) can be reduced by carrying out the electrolysis at an increased temperature. Temperatures of up to 300-400°C are possible when working with molten alkali hydroxides. At elevated temperatures, however, corrosion of electrode and separator materials becomes pronounced. For example, asbestos in the form of woven cloth, mat or felt is an ideal separator material below 100°C in an alkaline environment, but it fails at temperatures of over 100°C due to its enhanced dissolution in strong alkaline environment.

2.3.3 Electrode Overpotentials

The difference in electrode potential at any specific current density and the theoretical reversible potential is called the overvoltage at that current density. The greater the current, the greater the overpotential and the greater the irreversibility of the electrode process. The overpotential for an electrode reaction is given by the Tafel equation:

$$\eta = a + b \log i \qquad (13)$$

where

$$a \text{ is } \mp (2.303 \frac{RT}{\alpha nF}) \log i_o, \; b \text{ is } 2.303 \frac{RT}{\alpha nF},$$

α = transfer coefficient, i_o is the exchange current density and i denotes either anodic or cathodic current. The values of a and b are characteristic of each electrode process.

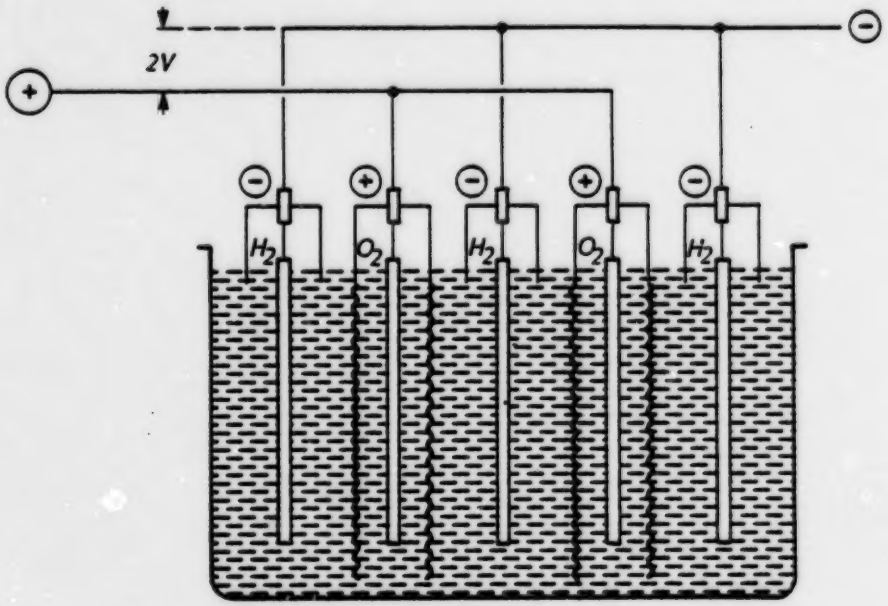
Both the electrode processes in the electrolysis of water are highly irreversible and have high overpotentials on all practical electrode materials. The hydrogen or oxygen overvoltages strongly depend on the nature of the electrode material, ions present at the interphase, reaction mechanism, temperature, ageing and porosity.

Since different electrode materials are suitable and acceptable as anode or cathode materials in different types of electrolyzers, a detailed account of electrode overpotentials will be given later.

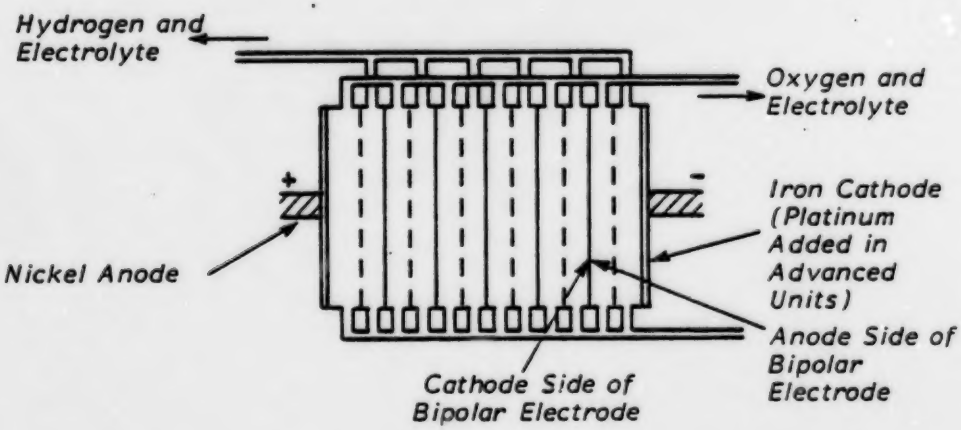
Porous electrodes provide a higher specific surface at the phase boundaries for electrochemical reactions. Thus with a porous electrode, significantly lower effective current densities can be attained compared to nonporous electrodes at any electrode potential. Moreover, porous electrodes offer the flexibility of design so that gas bubbles being produced at the electrode-electrolyte interface can be channeled away from the interelectrode space.

3.0 BASIC DESIGNS OF ELECTROLYZER CELLS

(a) Monopolar Electrolyzers: These cells use a series of anodes and cathodes alternately suspended vertically and parallel to one another in a tank partially filled with electrolyte. Alternate electrodes, usually cathodes, are surrounded by diaphragms that prevent passage of gas from one electrode compartment to another (Figure 3). This



Schematic Diagram of a Unipolar (Tank-type) Electrolyzer


Hydrogen and Electrolyte
Oxygen and Electrolyte
Iron Cathode (Platinum Added in Advanced Units)
Nickel Anode
Anode Side of Bipolar Electrode
Cathode Side of Bipolar Electrode

Filter-press (Bipolar) Cell Construction

FIGURE 3

BASIC DESIGNS OF ELECTROLYSER

arrangement allows an individual tank to operate with a 1.9 to 2.5 V power supply. Because of possible high currents at these cell voltages, the cost of electrical conductors is high.

Electrolyser Corporation is the only user of this design in its Stuart cell.

(b) Bipolar Electrolyzers: More recent electrolyzer designs use stacks so that the positive electrode of one cell is directly connected to the negative electrode of the next cell (Figure 3). An assembly of cells has a superficial resemblance to a filter press because the electrolyte is manifolded to flow through each cell in parallel while O_2 and H_2 exit lines are similarly manifolded through the stack.

Because the cells of the filter press type electrolyzer can be relatively thin, a large gas output can be achieved from a relatively small piece of equipment. It is usually necessary to cool the cells by circulating the electrolyte through them and the exiting electrolyte carries the product gases with it. Before recycling the electrolyte, the gases must be removed.

4.0 TYPES OF ELECTROLYZERS

Commercial electrolyzers as well as those under development, can be classified into the following four categories, based on the electrolyte employed:

1. Alkaline Electrolyzer
2. Solid Polymer Electrolyte (SPE) Electrolyzer
3. Vapour Phase Electrolyzer Using Ceramic Oxide Ion Conductors
4. Vapour Phase Electrolyzer Using Ceramic Proton Conductors

5.0 Alkaline Electrolyzer

Most commercial electrolyzers are alkaline electrolyzers of either Unipolar or Bipolar design. They use low cost materials and operate at about 2 - 2.5 V. Hydrogen and oxygen overvoltages contribute significantly to this cell voltage (Figure 2).

5.1 Hydrogen Overvoltage

Mild steel or nickel are the most common cathode materials. Hydrogen overvoltage on mild steel is ~400 mV at a current

density of ~100 mA/cm^2 and 25°C/5/. The reduction of this large overvoltage remains one of the major objectives around the world.

The hydrogen overvoltage contribution to the measured cell voltage is determined by the Tafel equation (Equation 13). The transfer coefficient α and the exchange current density i_o are characteristic of the electrode material.

The mechanistic and electrocatalytic aspects of the hydrogen evolution reaction have been extensively investigated. The kinetic data pertinent to the alkaline solutions have been compiled in Table II/4/. A periodic variation of hydrogen overvoltage with atomic number, work function etc, is observed. Ni, Pd and Pt with d^8s^2, $d^{10}s^0$ and d^9s^1 electronic configurations, respectively, exhibit minimum hydrogen overpotential while Zn, Cd and Hg with $d^{10}s^2$ electronic configuration show maximum value/4/.

Most extensive investigations were carried out on various nickel based materials (eg, alloys, intermetallic compounds and interstitials), since nickel is a reasonably stable material in alkaline solutions and is relatively inexpensive. Polarization data on smooth nickel electrodes (Figure 4) show marked variation of the kinetic parameters with temperature. Exchange current density i_o changes from 2 x 10^{-4} A/cm^2 at 80°C to 4 x 10^{-2} A/cm^2 at 264°C and α = 0.05. Changing of Tafel slope (b in Equation 13) with potential and temperature suggests that the electrochemical desorption mechanism is operative on Ni in alkaline solutions at high temperatures/4/.

Comparison of the i_o values on various forms of Ni (Figure 5) shows that high i_o and hence low overpotentials can be achieved by effectively utilizing the high surface area of porous electrode structures.

One of the problems observed during the usage of Ni-based cathodes for water electrolysis is the loss of activity as indicated by the time variation of the cathode potential. Data from a galvanostatic investigation/6/ is presented in Table III. The cathode overpotential increases by 200-500 mV over a six hour period depending on the current density. The activity of the electrodes could be completely recovered by shorting the anode to cathode for a brief time (~15 minutes) or by simply leaving the electrodes at open circuit for a longer period/4/.

TABLE II/a/

KINETIC PARAMETERS FOR THE H_2 EVOLUTION REACTION FROM ALKALINE SOLUTIONS

Metal	Concentration	Temperature °C	- log i_o A/cm^2	Tafel slope, mV
Ag	6 N NaOH	25	6	120
Al	6 N NaOH	25	4.52	140
Au	0.1N NaOH	25	5 - 7	71 - 120
Sb	6 N NaOH	25	6	150
Carbon	40% NaOH	60	3.982	167
Co	6 N NaOH	25	4.3	140
	1 N NaOH	25	2.26	145
Cu	6 N NaOH	25	5.3	160
Cd	6 N NaOH	25	6.398	160
Cr	6 N NaOH	25	7	120
Fe	6 N NaOH	25	4	150
Mg	6 N NaOH	25	5.523	350
Mo	6 N NaOH	25	5	140
Mn	6 N NaOH	25	7.52	120
Nb	1 N NaOH	25	7.5	140
Ni	6 N NaOH	25	5	140
	50% KOH	80	3.959	140
	50% KOH	150	3.745 - 2.022	54 - 280
	50% KOH	208	3.097 - 1.699	70 - 320
	50% KOH	264	3.032 - 1.699	66 - 200
Pb	6 N NaOH	25	5.398	250
Pd	0.1 N NaOH	25	5.0	125
Pt	0.5 N NaOH	25	4.06	117
Ir	0.1 N NaOH	25	3.26	125
Rh	0.1 N NaOH	25	4.0	118
Sn	6 N NaOH	25	5.52	230
Ta	6 N NaOH	25	6.523	150
Ti	6 N NaOH	25	6	140
W	1.0 N NaOH	30	6.6 - 5.56	59 - 98
Zn	6 N NaOH	25	6.398	210
Zr	6 N NaOH	25	6.523	220
Alloys and Compounds				
Stainless Steel				
304	1.0 M NaOH	25	5.09	133
	3.0 M NaOH	25	5.14	121
	5.0 M NaOH	25	5.71	115
	10.0 M NaOH	25	5.38	105
	6 M NaOH	25	5	120
Ni	0.1 N NaOH	25	5.4	130
Ni -12 at %Pd	0.1 N NaOH	25	4.82	115
Ni -35 at %Pd	0.1 N NaOH	25	4.5	130
Ni -68 at %Pd	0.1 N NaOH	25	3.49	130
Pd	0.1 N NaOH	25	3.46	110
Ni	0.1 N NaOH	25	5.35	130
Ni -25 at %Pt	0.1 N NaOH	25	5.0	155
Ni -50 at %Pt	0.1 N NaOH	25	4.02	170
Ni -63 at %Pt	0.1 N NaOH	25	3.89	120
Pt	0.1 N NaOH	25	3.40	120
Pt <5% V	0.1 N NaOH	25	5.0	158
Pt <5% Mo	0.1 N NaOH	25	5.75	165
TiC	0.1 N NaOH	25	6.52	140
TaC	0.1 N NaOH	25	4.7	300
B_4C	0.1 N NaOH	25	5.7	135
TiC (97%)+Ni(3%)	42.2% NaOH	70	2.667	141
	42.2% NaOH	80	2.538	145
	42.2% NaOH	90	2.359	153
Fe -75%Ni	0.1 N NaOH	25	5.46	115
Zn	9 N KOH	25	8.824	124

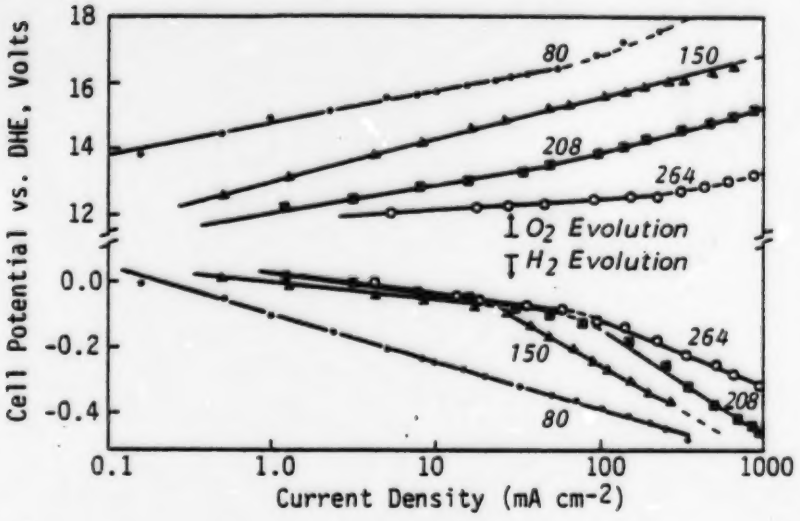


FIGURE 4

POLARIZATION DATA FOR H_2 AND O_2 EVOLUTION REACTIONS ON POLISHED NICKEL ELECTRODES IN 50 wt% KOH AT 80, 150, 208, AND 264°C /4/

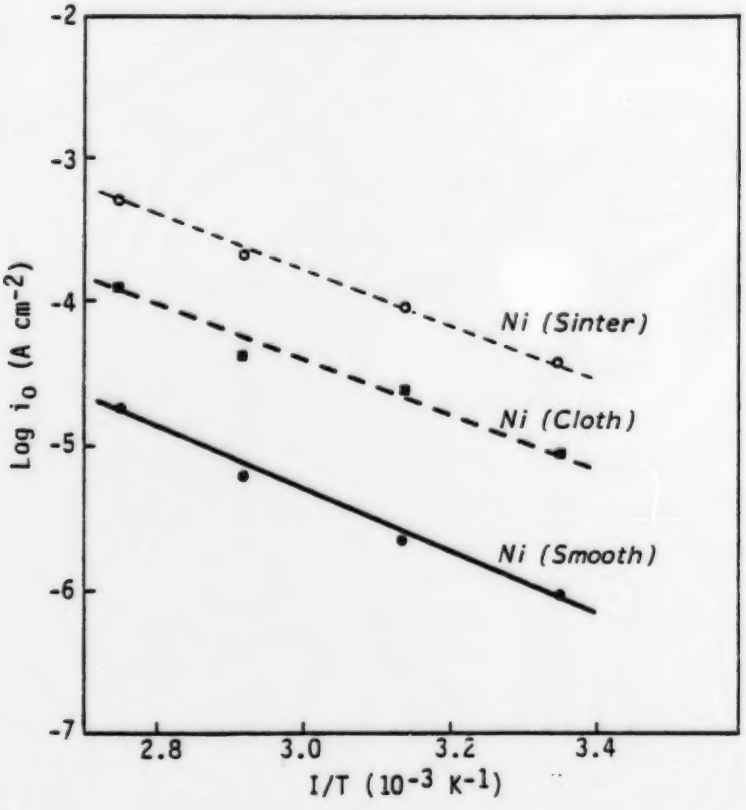


FIGURE 5

ARRHENIUS PLOTS FOR EXCHANGE CURRENT (SMOOTH ELECTRODES) OR APPARENT EXCHANGE CURRENT (CLOTH AND SINTER ELECTRODES) FOR THE HYDROGEN EVOLUTION REACTION ON Ni ELECTRODES IN 34% KOH/4/

TABLE III/6/

TIME DEPENDENT ENERGY EFFICIENCY LOSSES AT Ni CATHODES IN ALKALINE WATER ELECTROLYSIS SYSTEM

C.D. mA/cm^2	Initial Cathode Potential V vs SCE	Final Cathode Potential V vs SCE	$\Delta E(V)$
10	-1.472	-1.696	0.224
25	-1.518	-1.827	0.309
50	-1.547	-1.967	0.420
100	-1.555	-1.994	0.439
200	-1.596	-2.093	0.497

A number of new electrocatalysts have been tested for hydrogen evolution. Some of the promising ones include: $NiCo_2S_4$, Ni_2B, electrodeposited iron on Ni, Raney nickel and mixed metal oxides with metallic ratios 2Ni-1Co, 5% Mo and 2Ni-1 Co-5% Cu/7/.

5.2 Oxygen Overpotential

O_2 evolution is one of the most important fundamental anodic processes in electrochemistry and is highly irreversible as is evident from the large overvoltages required on most electrodes even at low current densities. Progress in the study of the electrochemical kinetics of O_2 evolution and hence the development of new, more efficient catalysts has been slow because of the complexity of the electrochemical reaction. Some of the factors responsible for the slow progress are/8/:

i) Role of anions: The mechanism by which anion adsorption affects the rate of reaction is not well understood.

ii) Anodic dissolution of metals and oxides: The interpretation of the overvoltage data is complicated by the co-occurrence of the anodic dissolution of metals and metal oxides and the transition of metal and metal oxide surfaces from active to passive regions.

iii) Formation of oxide films of different compositions: Uncertainties about the formation of stoichiometric oxide on the electrode surface and the slowness of obtaining constant overvoltage are responsible for large discrepancies in the overvoltage data obtained by different authors.

iv) Distribution of inner potentials in the oxide films and the ionic double layer: The presence of the oxide on the metal electrode surface changes the distribution of inner potentials as shown in Figure 6. The discharge occurs at interface IIIb - II as compared with I - II (in the case of bare metal surface). In the presence of poorly conducting oxide coatings the potential drop across I - IIIb cannot be ignored and the potential difference $\phi I - \phi IIIb$ must be subtracted from $\phi I - \phi II$ before the latter can be introduced in kinetic equation. The problem of this correction becomes even more complicated by the fact that the type of oxide and its thickness changes with current density (ie, potential) and time.

These factors are responsible for a gradual decrease in current density at a constant anode potential over a period of years on Ni as well as Pt electrodes/9/.

Recent kinetic data for the O_2 evolution reaction on various metals, alloys or intermetallics, and pure and mixed oxide surfaces is presented in Table IV/4/. It shows that nickel based materials are probably the best catalyst surfaces for the oxygen evolution reaction in alkaline media. Comparison of smooth and porous electrodes/10/ shows similar polarization behaviour, unlike the case of H_2 evolution. This suggests ineffective utilization of the internal surface area of the porous body, presumably due to the blockage of the surface by gas bubbles from the bubble morphology effects involved in gas evolution kinetics. The optimized electrode structures reported so far include sintered Ni electrodes impregnated with nickel oxide, anodized nickel surfaces, NiOOH, high surface area $NiCo_2O_4$ electrodes, and 50 Ni-50 Fe alloys.

Nickel or nickel plated mild steel is the most commonly employed anode material. The most generally accepted mechanism/4/ for O_2 evolution on nickel surface in alkaline media involves the following steps:

$$OH^-_{ads} \overset{\rightarrow}{\leftarrow} OH_{ads} + \bar{e} \qquad \text{(i)}$$

$$OH^- + OH_{ads} \overset{\rightarrow}{\leftarrow} O_{ads} + H_2O + \bar{e} \qquad \text{(ii)}$$

$$O_{ads} + O_{ads} \overset{\rightarrow}{\leftarrow} O_2 \qquad \text{(iii)}$$

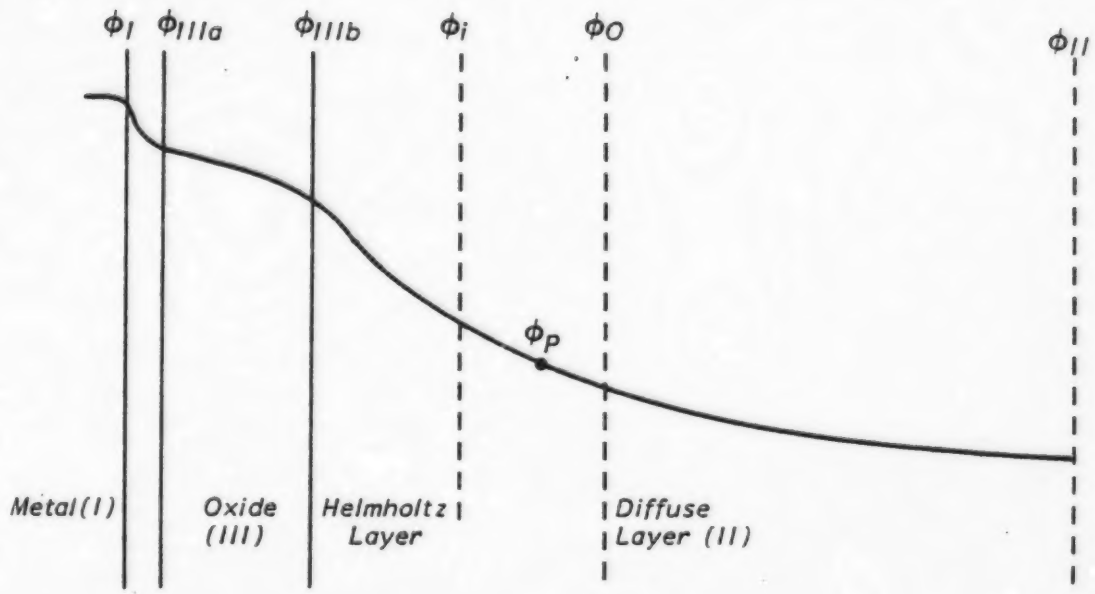


FIGURE 6

DISTRIBUTION OF INNER POTENTIALS AT THE INTERFACE METAL (I) - OXIDE (II) - SOLUTION (III)/8/.

TABLE IV/4/

KINETIC PARAMETERS FOR THE OXYGEN EVOLUTION IN KOH SOLUTIONS

Material	Temperature, °C	KOH, wt %	Tafel slope, V		Transfer coefficient[a]		Exchange current density, A/cm^2	
			Low η	High η	Low η	High η	Low η	High η
Pt	80	30	0.046		1.5		1.2×10^{-9}	
Ir	80	30	0.055		1.3		5.0×10^{-8}	
Rh	80	30	0.067		1.0		3.8×10^{-7}	
Ru	80	30	0.067		1.0		3.0×10^{-8}	
Os	80	30	0.070		1.0		1.0×10^{-7}	
Pd	80	30	0.067		1.0		1.9×10^{-7}	
Ni	80	30	0.062		1.1		2.3×10^{-7}	
	80	50	0.095		0.74		4.2×10^{-6}	
	150	50	0.125		0.67		1.8×10^{-4}	
	208	50	0.085	0.135	1.1	0.71	6.0×10^{-4}	3.5×10^{-3}
	264	50	0.032		3.3		1.0×10^{-3}	
Co	80	30	0.126		0.56		3.3×10^{-6}	
Fe	80	30	0.191		0.37		1.7×10^{-5}	
75 Ni-25 Ir[b]	80	30	0.067		1.0		8.8×10^{-7}	
50 Ni-50 Ir[b]	80	30	0.047	0.086	1.5	0.81	3.4×10^{-8}	2.0×10^{-5}
25 Ni-75 Ir[b]	80	30	0.064		1.1		6.0×10^{-7}	
75 Ni-25 Ru[b]	80	30	0.056		1.3		2.4×10^{-8}	
75 Ni-25 W[b]	80	30	0.114		0.61		4.6×10^{-5}	
50 Ni-50 W[b]	80	30	0.125		0.56		2.5×10^{-4}	
Ni_3Ti	80	30	0.064		1.1		4.7×10^{-7}	
NiTi	80	30	0.057	0.094	1.3	0.74	6×10^{-6}	2.8×10^{-5}
$NiTi_2$	80	30	0.383		0.18		6.5×10^{-5}	
TiO_2 + 30 mol % Pt Oxide	80		0.225		0.31		9.5×10^{-6}	
TiO_2 + 30 mol % Co Oxide	80	30	0.193		0.36		2.0×10^{-6}	
TiO_2 + 30 mol % Ni Oxide	80	30	0.259		0.27		1.4×10^{-4}	
TiO_2	80	30	0.118		0.59		7.3×10^{-9}	
TiO_2 + 30 mol % RuO_2	80	30	0.068		1.0		6.4×10^{-7}	
TiO_2 + 100 mol % RuO_2	80	30	0.066		1.1		2.5×10^{-6}	
$NiCo_2O_4$	80	30	0.042		1.67		2.9×10^{-8}	

a Transfer coefficient = 2.303 RT/bF, where b is the Tafel slope.

b In atom percent.

where one of the charge transfer steps is rate controlling. Observed dependence of transfer coefficients and Tafel slope suggest a slow electron transfer step at low temperatures and a slow recombination step at high temperatures on nickel electrodes in 50 wt% KOH solutions/4/.

Srinivasan et al/9/ conducted an extensive study to investigate the reasons for the performance degradation of an Ni anode. Using ellipsometeric and electrochemical techniques, they have concluded that the decay in current at constant potential or the increase in potential at constant current is related to the gradual conversion of Ni^{3+} to Ni^{4+} ions on the surface of nickel oxide. The ratio of Ni^{3+} to Ni^{4+} ions is strongly dependent on anodization potential and polarization time. However, if after anodizing at higher potentials the nickel anode is brought down to 1.5 V, the catalytic activities of aged electrodes are regained/9/. Ellipsometeric studies have shown that the rejuvenation of aged oxide films is essentially the recovery of active Ni^{3+} sites on the very top layer of the films. Binary, ternary and higher oxides of various crystal structure types are being developed that have stable reactive cationic species on the surface of the oxide layer/7/. Based on the crystal structure, these new catalysts can be divided into the following categories:

i) Spinel-type Oxides: $NiCo_2O_4$ has been shown to give promising results/11,12/. Other compounds studied under this category include Co_3O_4/13,14/.

ii) Perovskite-Type Oxides: $NiLa_2O_4$/15/ and $LaNiO_3$/16/ have been shown to be stable and possess higher electrochemical activity for O_2 evolution. Other compounds investigated include $La_{1-x}A_xCoO_3$ where A stands for Ba or Sr, $La_{1-x}Sr_xMnO_3$, $SrFeO_3$, $La_{1-x}Sr_xCoO_3$ and $SrFe_{0.9}M_{0.1}O_3$ where M stands for Ni, Co, Ti or Mn/7/.

Tseung et al/11/ have shown that the doping of nickel oxide with lithium reduces the increase in oxygen overvoltage with time. This improvement in performance is attributed to the decreased resistivity of the doped material (100 ohm·cm as compared with 10^8 ohm·cm for NiO_2). More recently, Tseung and co-workers/12/ have shown that the most important criteria governing the choice of oxides for the oxygen evolution is the equilibrium potential of the metal/metal oxide or the lower metal oxide/higher metal oxide couple, if there is more than one form of oxide. According to their hypothesis this equilibrium potential must be reached before O_2 evolution can take place. This implies that the final step in oxygen evolution on a metal or metal oxide surface is the decomposition of an unstable higher oxide. Using

this criterion, spinel $NiCo_2O_4$ has been found to be a suitable material for oxygen evolution/12/. Higher oxide formation on this material is shown to be limited to the surface only where it decomposes to form lower metal oxide releasing oxygen. Most spinels contain cations in two or more oxidation states, the common general formula being XY_2O_4/13. The mixed valences of the cations help in the reversible adsorption of O_2 by providing donor acceptor sites for chemisorption/14/. New macrocycle based electrocatalysts are being developed for bifunctional oxygen electrodes.

5.3 Ohmic Overpotential - Separators

Several materials have been examined (see Table V) for use as diaphragms and the following appear promising at temperatures >100°C in alkaline solutions.

(a) Teflon-based cation exchange membranes (Nafion) in 20% NaOH solutions at 120-160°C. However, their resistivity is higher in >20% NaOH solutions.

(b) Teflon-bonded potassium titanate. Its resistivity is independent of the nature of the electrolyte and has proven stability for over 5000 hours. However, it appears to embrittle in regions that are not in contact with the electrolyte.

(c) Asbestos treated with a binder (eg, tin hydrosol) or in NaOH solutions containing sodium silicate.

(d) Polysulfone fabricated in thin fiber form.

The alkaline electrolyte level is controlled automatically by an external float control chamber and valve. Both the H_2 and O_2 gases, largely separated from the electrolyte within the cell tank, enter individual gas cooler-condenser-demister immediately above the cells. All entrained electrolyte and condensed water vapours return to the cell tank by gravity flow. Electrolyte circulation in the cell is achieved automatically by the upward movement of gas bubbles.

5.4 Commercial Alkaline Electrolyzers

A number of alkaline electrolyzers are available on the market, in sizes of up to 95 tonnes of H_2 per day. Performance characteristics of different electrolyzers are compared in Table VI. Important features of different electrolyzer technology are as follows:

TABLE V/4/

AN ANALYSIS OF THE USEFULNESS OF VARIOUS TYPES OF MATERIALS AS SEPARATORS FOR ALKALINE WATER ELECTROLYSIS AT TEMPERATURES IN THE RANGE 80 - 150°C

Materials - Class or Type	Comments
Asbestos material	Ideal separator under 100°C in alkali
Woven material	Asbestos works well; used commercially. Boron nitride - not stable in alkali especially above 100°C.
Potassium titanate paper (Teflon binder)	Very good in alkali above 100°C.
Nafion	Very good in acid at all temperatures; works well in 20% NaOH at 100°C and above.
Nonwoven (felts)	Low-resistance material but limited life at elevated temperature. Also possible higher diffusion of gases.
Battery separator	Works well as separator material. Most are of polyethylene base - not suitable for higher temperature.
Cationic membrane	With the exception of Nafion, found to be suitable in regard to resistance but as a rule, short life above 100°C
Anionic membrane	Very high resistance and short life.
Porous membrane	Teflon base, excellent durability above 100°C. All have high resistance (2-10 times greater than asbestos).

TABLE VI [2,3]

TYPICAL CELL-OPERATING PARAMETERS

Manufacturer:	The Electrolyser Corp., Ltd	Brown Boveri & Cie	Norsk Hydro A.S.	DeNora S.P.A.	Lurgi GmbH
Cell Type:	Monopolar tank	Bipolar filter press	Bipolar filter press	Bipolar filter press	Bipolar filter press
Operating pressure:	Ambient	Ambient	Ambient	Ambient	3100 kPa
Operating temperature:	70°C	80°C	80°C	80°C	90°C
Electrolyte:	28% KOH	25% KOH	25% KOH	29% KOH	25% KOH
Current density, A/M^2:	1340	2000	1750	1500	2000
Cell voltage, V:	1.90	2.04	1.75 (after 1 yr operation)	1.85 (increases to 1.95 after 2 yr)	1.86
Current efficiency, %:	>99.9	>99.9	>98	~98.5	98.75
Oxygen purity, %:	99.7	≥99.6	99.3-99.7	99.6	99.3-99.5
Hydrogen purity, %:	99.9	≥99.8	98.8-99.9	99.9	99.8-99.9
Power consumption, DC-kWh per normal m^3 H_2:	4.9	4.9	4.3	4.6	4.5

Note: Current required for 1 nm^3 hydrogen = 2393 A hr.

5.4.1 The Stuart Cell/3,4/

Named after its inventor A. Th. Stuart, this cell is manufactured by the Electrolyser Corporation Ltd, a Canadian Company which is the only manufacturer of monopolar tank cells. Electrolyser Corporation has been in the electrolyzer business for 50 years and has 500 electrolyzers installed in about 80 countries.

Stuart cell has gained a reputation for reliability and low maintenance. It consists of an all welded, rectangular, low carbon steel tank, nickel plated on the inside for additional corrosion protection. A nickel plated gas tight cover supports the oxygen collecting chamber, asbestos cloth separators and the electrodes. The electrodes are made of high conductivity steel. The anodes are plated with a heavy sponge nickel and the cathodes are specially treated to generate a more active surface for low cathodic overvoltage. All electrodes are suspended and isolated from the cover. All anodes are connected together to a bus bar, as are all cathodes. Because of the parallel connection, the cell voltage is ~1.9 V.

Each anode is surrounded by a woven asbestos cloth diaphragm to prevent mixing of the product gases and guide the generated O_2 to the oxygen chamber located immediately below the cell cover. Hydrogen generated on the cathodes rises between, but outside, the diaphragms to the hydrogen compartment under the cover.

Stuart cells operate at ambient pressures and at 70°C using 28% KOH as the electrolyte. The temperature of the cells is controlled by regulating water flow to a cooling jacket on one side of the cell.

Current Developments

Both, cell improvements and total hydrogen plant developments are possible in the Stuart cells. An increase in operating temperature from 70 to 90°C is expected to increase the overall thermal efficiency by lowering the operating voltage. Replacement of the present asbestos diaphragms may be necessary for higher temperature operation. Development of new, more efficient electrocatalysts can reduce the cell potential significantly.

Electrolyser Corp is actively engaged in developing its monopolar technology to produce hydrogen at costs comparable to that projected for SPE technology. Advanced versions of the Stuart cell are projected to operate at cell voltages of ~1.74 V (at 134 mA/cm^2) compared to the present value of 1.90 V, at an energy efficiency of 87%. Nickel boride based cathodes and

$NiCo_2O_4$ coated anodes are being tested for potential application in future electrolyzers/17/.

Generation II cells are being tested in Hydro Quebec. Tests on an advanced version of a 35 MW plant will start soon.

5.4.2 Brown Boveri and Cie (BBC) Technology/3,4/

BBC electrolyzer technology uses bipolar cell design and is highly modularized so that standardized cell components such as cell frames, electrodes and diaphragms allow construction of cells with a wide variation in generation capacity. More than 800 of these electrolyzers have been built, the largest installation being at Aswan, Egypt. Standard units producing from ~5 to 300 m^3/hr are currently manufactured. Any number of these electrolyzers can then be assembled in a suitable series - parallel electrical arrangement to supply the total desired hydrogen output.

The electrolyzer may contain up to 80 unit cells with a cell voltage across each unit cell of about 2 V. A woven asbestos diaphragm is stretched in each cell frame, which in turn is pressed between insulating frame gaskets on both sides of the centre plate. Pre-electrodes are mounted on both sides of the centre plate. The anode is nickel plated steel supplied with or without an activated surface. The activated surface of the cathode is reported to last only a few years. Several such frame and electrode elements can be mounted together between a pair of end plates.

A forced electrolyte circulating system feeds the alkaline solution via a header into each half of the cell frame. A mixture of electrolyte and the respective gas leaves each half of every cell frame through its external gas outlet and then through a dip pipe into the gas separator which also acts as a cooler of the separated electrolyte to maintain the cell at a constant temperature. The inlet and outlet pipes from each cell frame are of pure Ni and lengths of plexiglass are used to insulate these pipes and thereby minimize parasitic currents.

Current Developments

BBC is aiming at enhancing the electrolyzer efficiency by using better electrocatalysts/3/. Higher capacities with single modules are planned by increasing the current density from 200 to 340 mA/cm^2.

5.4.3 Norsk Hydro A.S. Technology/3,4/

The Norsk Hydro Electrolyzers are of the bipolar filter press type. The electrolyte feed and the gas-electrolyte outlet are

through ducts within the filter press frames with small bore holes from the ducts into and out of each cell chamber. A series of identical gas producing cells are firmly pressed together between two solid end frames. A typical electrolyzer has about 235 unit cells, each with a cross-sectional area of electrodes of 2.1 m^2, capable of carrying 3600 A and generating 350 m^3 of H_2 per hour.

In individual cell construction, the electrodes, gaskets and a diaphragm are sandwiched together to form two separate compartments for the generation of H_2 and O_2 gases. The main support electrode is common to two neighboring cells, with perforated plate fore-electrodes fastened by rivets or screws to each side of the main electrode. Distance between the fore electrodes and the main support electrode is maintained in order to allow free passage of gases.

Asbestos cloth reinforced with nickel wire is used as a diaphragm. On each side of this diaphragm frame there are small passages into one of the diaphragm rings. The upper gas-electrolyte ducts terminate in two gas separators at the front of the electrolyzer.

All metal parts including the electrodes are made of mild steel. The anodes are coated with active nickel which degrades after a number of years.

Current Developments

In house developments include new diaphragms and improved cell designs for operation at higher loads. In a joint venture with Electricitè de France new electrocatalyst coatings are being developed and evaluated.

5.4.4 Lurgi Gmbh Technology/3,4/

This bipolar filter press design operates at 3100 kPa. The high pressure operation results in the lowering of the cell voltage (Table VI). Further cost savings are realized because no gas compressors are needed. The electrolyte feed and gas electrolyte outlet system are similar to Norsk Hydro cell.

Nickel plated wire and activated gauge electrodes are laid directly on the 3 mm thick asbestos board diaphragms. The electrodes are then pressed against the asbestos diaphragm by the embossed cell partition wall. The embossed or dimpled nickel-plated steel plates fixed into the cell frames provide electrical contact between the wire mesh anodes and cathodes of adjoining cells and also permit the H_2 and O_2 gas bubbles to rise behind the electrodes. Each cell frame is separated and sealed by a teflon-covered gasket.

A number of cell modules can be assembled together and held between end plates. Electrolyzers of a wide range of capacities are supplied. The largest unit consisting of 350 unit cells has a current capacity of 6000 amps and can produce ~800 m^3 of H_2 per hour.

5.4.5 DeNora S.P.A. Technology

DeNora electrolyzer is a bipolar filter press design and consists of a number of bipolar elements assembled between two end plates by means of tie rods. The most famous DeNora electrolyzer is at Nangal in India.

The bipolar unit cell consists of a 5 cm thick steel frame surrounding a bipolar plate. Expanded planar metal electrodes are connected on both sides. Anodes and cathodes are both of nickel plated mild steel activated by a proprietary sulfide process. The activation lasts only about 2-3 yrs. However, the electrodes can be removed and reactivated. Use of expanded metal for electrode fabrication increases the available electrode area and facilitates the withdrawal of gases from the interelectrode gap.

A unique feature of the DeNora electrolyzer is the use of a double-woven, specially treated asbestos diaphragm. These are in physical contact with each other with the space between vented to the atmosphere. During normal operation, the diaphragms are pressed against one another but any penetration of gas bubbles results in the formation of a larger bubbles between the diaphragms, which is vented to the outside.

DeNora electrolyzers are supplied in standard sizes of 2500, 4500 and 10-12000 A, with the number of bipolar elements varying from 40 to ~100.

Current Developments

DeNora is actively engaged in developing novel (ruthenium and rhenium deposited on Fe) electrodes for use as cathodes and Ni(or Co), stainless steel-coated Ni, or Ni-Fe as anodes to lower the unit energy consumption.

5.4.6 Life Systems, Inc Technology/3,4/

The static feedwater electrolysis system developed by Life Systems, Inc., under NASA sponsorship, has potential applicability for terrestrial hydrogen production. It uses (a) an alkaline electrolyte; (b) a method whereby the electrolyte is retained in a thin, porous matrix, eliminating bulk electrolyte; and (c) a static water feed mechanism.

In the static water feed system, the water to be electrolyzed is supplied to the cell electrolyte as a vapour. Each cell is divided into three main compartments: a water-feed compartment, a hydrogen-gas compartment, and an oxygen-gas compartment. Compartment separation and liquid-vapour phase separation are achieved by the capillary action provided by liquid-filled asbestos sheets. Catalyzed porous-nickel plaques support the cell matrix, forming a composite electrolysis site. Plastic screens similarly support the water feed matrix.

The cell configuration is given in schematic form in Figure 7. When power is applied to the electrodes, water in the cell electrolyte is consumed. As a result, the concentration of the electrolyte increases, causing its vapour pressure to drop below that of the feed-compartment. This difference in vapour pressure is the driving force that causes the water vapour to diffuse across the hydrogen cavity to the cell matrix.

Life Systems utilizes a bipolar filter press construction with welded bus bars providing intercell current connection.

A major portion of the cell's inefficiency occurs at the anode which results in waste heat. Cell coolant passages are placed directly over the bipolar plate opposite the oxygen cavity. If air cooling is desired, the plate is extended out past the cell frame forming fins for convection or forced air cooling.

Because Life Systems electrolyzers were developed for space applications, expensive materials were utilized to provide reliability and efficiency. The system cell frames are injection moulded from a flame resistance plastic. All metallic parts are made from nickel alloy, which is then gold plated. Both, the feed water matrix and the cell matrix are made of Life Systems reconstituted asbestos.

The present Life System cell is designed to withstand pressures up to 4100 kPa and temperatures up to 104°C at a current density of 6500 A/m^2 and cell potential of 1.84 V. Future projections are for a cell operating at 14000 kPa and 150°C at a current density of 16,200 A/m^2. The cell potential under these conditions is projected to be 2.02 V.

5.4.7 Teledyne Energy Systems Technology/3,4/

Teledyne's cell design is quite unique since only one electrode is flooded with the electrolyte. The electrolysis cell contains the porous electrodes separated spatially and electrically by a piece of porous asbestos board or paper saturated with a 25% KOH solution. The porous wetted asbestos matrix has a pore diameter of about 0.7 μm, which precludes gas flow directly from the

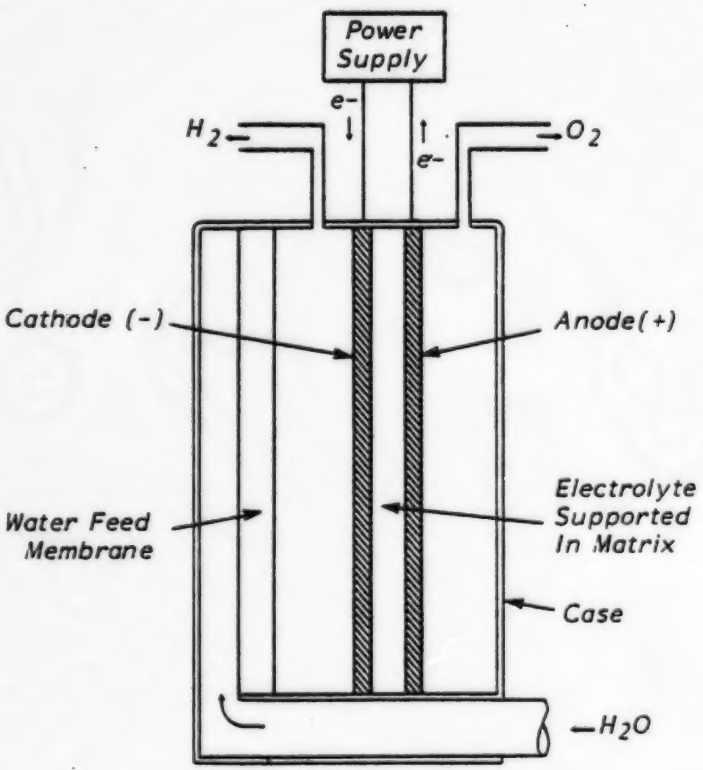


FIGURE 7
LIFE SYSTEMS CELL CONFIGURATION/3/

cathode to the anode. This property of the asbestos matrix allows the cell to operate with the hydrogen gas pressure higher than the oxygen gas pressure and still ensures that all the free liquid remains within the anolyte compartment of the cell. The hydrogen is generated in a liquid free compartment. Only one electrolyte-gas separator, electrolyte tank, cooler and pump is required.

Two series of Teledyne electrolyzers are available; HG Series with a capacity of 0 - 60 l/hr of H_2 at STP and HS Series with a hydrogen generating capacity of 1200 - 12,000 l/hr at STP.

Current Developments

Advanced Teledyne Electrolyzers are being developed to reduce the power consumption for H_2 production. Current research efforts include: development of materials for cell frame to stand operation at higher temperatures, development of various thermoplastic separators to allow higher differential pressures, development of new cathode materials (Ni_2B - coated Ni screen and a proprietary cathode with Pt) to replace Ni screens presently used.

5.5 Summary

Alkaline electrolyzer technologies are well established. A number of these are commercially available in different sizes ranging up to 95 tonnes of H_2 per day. All the materials used are low cost so the capital cost of electrolyzers is low. Compared to new technologies the energy efficiencies of alkaline electrolyzers are low. Although intensive efforts are in progress to lower the activation overpotential and ohmic polarization, the extent to which improvements in energy efficiency are possible seems limited. At this stage, the projected (ultimate) efficiencies of ~120% (based on Higher Heating Value of hydrogen) seem overly optimistic. Efficiencies of the order of 100% (ie a cell potential of ~1.5 V) may be achieved during the next two decades.

For any application involving tritium, alkaline electrolyzers appear unsuitable due to the large tritium inventories required. A reduction in inventory is possible by cell design improvements, however, it seems unlikely that it will compete favourably with the vapour phase electrolyzer technologies.

6.0 SOLID POLYMER ELECTROLYTE ELECTROLYZER/18-21/

Solid polymer electrolyzer technology is an offspring of the Solid Polymer Electrolyte (SPE) fuel cell technology that was developed for the space program. General Electric is presently marketing small electrolyzers based on SPE technology with a hydrogen generating capacity of 2.8 - 9.1 m^3 per hour. The electrolyzers are suitable for laboratories and instrumentation where high purity hydrogen is desired. Larger systems are being developed for life support regenerative systems in naval, submarine and select commercial applications. Sponsored by the US Department of Energy, Niagara Mohawk Power Co, Empire State Electric Energy Research Corp and General Electric Co, a program is underway to design and field test a 58 MW (17,700 m^3H_2 per hour) hydrogen plant.

Primary features of the SPE system are:

- Cell can operate with high differential pressures (>3400 kPa) and high gas generating pressure (20,000 kPa) in properly designed system hardware.
- Electrolyte concentration is fixed and the electrolyte is not mobile in the system.
- No possibility of acid carryover into the effluent gas to corrode downstream system components.
- No corrosive electrolytes to control or leak in the system since water is the only circulating fluid.
- Electrolyte is essentially invariant in operation, resulting in minimum maintenance and cost.
- Highest efficiency of any available water electrolysis technology.
- Cell can operate at high current density (>20 kA/m^2) resulting in minimum size and cost.

A cross-section of a single cell used in water electrolysis is shown in Figure 8. The cell consists of a 0.2 - 0.3 mm thick sheet of membrane with high surface area catalytic electrodes attached and embedded on both sides. On each side of the structure, there are expanded metal screens which provide electronic conductivity as well as fluid distribution. The fluid compartments between the two cells are separated by a thin sheet of metal foil that allows the bipolar internal current collection. All components in the system are either spot welded or noble metal coated to minimize contact resistance problems.

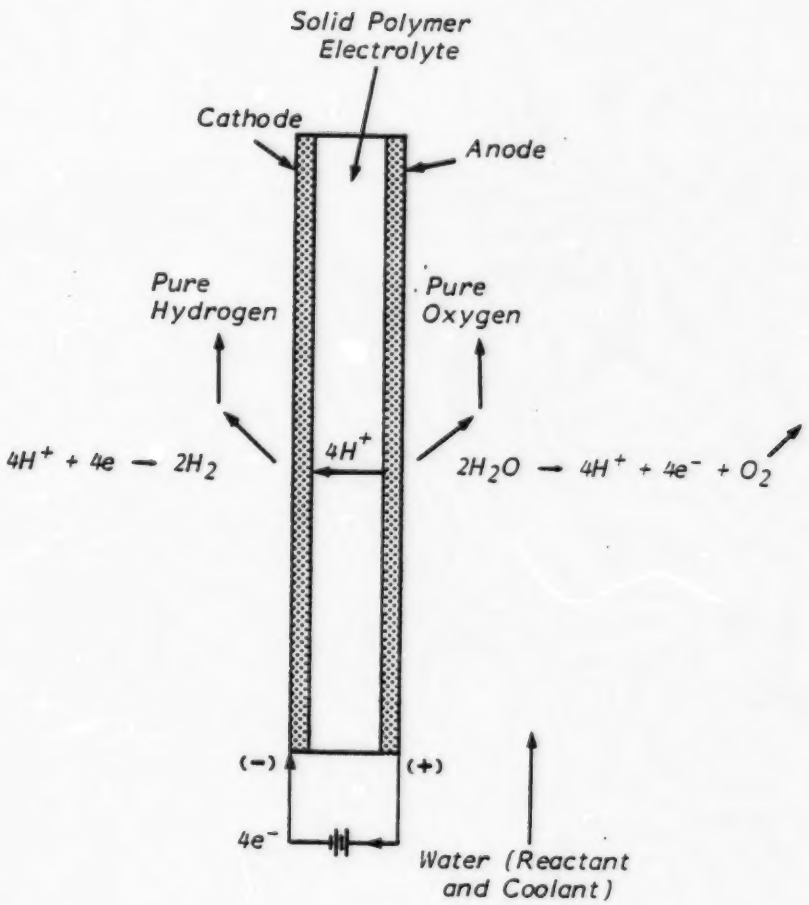


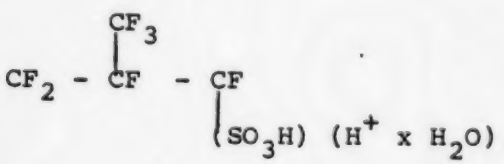
FIGURE 8
SPE ELECTROLYSIS CELL SCHEMATIC

Distilled water is supplied to the oxygen evolution electrode (the anode) where it is electrochemically decomposed to provide O_2, H^+ and electrons. H^+ ion moves through the membrane to the H_2 evolving electrode (the cathode) while electrons pass through the external circuit. Approximately 3.5 - 5 molecules of water are transported with each H^+ in a cell assembly whose membrane is water equilibrated at 100°C. Thus an excess of water has to be supplied to the anode compartment and the anodic output has to be recirculated to remove heat.

6.1 Components of the SPE Electrolyzer

6.1.1 Electrolyte

Development of the SPE technology has, so far, relied almost entirely on the use of Nafion membranes - a Dupont product. It is a perfluorinated sulfonic acid polymer having many of the physical characteristics of teflon/22/. When saturated with water, it is an excellent ionic conductor (<15 ohm·cm). No free acid or alkaline liquids are required in the system although the hydrated SPE itself is highly acidic with a pH equivalent of a 10 wt % H_2SO_4 solution. Chemically, the hydrated polymer approximates:



Conductivity is provided by the mobility of the hydrated hydrogen ion ($H^+ \times H_2O$) from one sulfonic acid group to the other. Since the position of the sulfonic acid groups is fixed, the concentration of the acid remains constant within the electrolyte.

The production process for Nafion is complex as reflected by the high cost (~400 US dollars/m^2). This high cost does not favour the competitiveness of the SPE technology with other electrolysis technologies. General Electric and other organizations have been developing and evaluating alternative ion exchange membranes/4,23/, including the perfluorocarboxylic acid membrane developed by Asahi Chemicals in Tokyo, Japan. No information is presently available on the performance of perfluorocarboxylic acid membrane.

The ultimate goal in developing alternate membranes for SPE water electrolysis system is to reduce the cost to ~1/8 th the current price of Nafion membranes. Radiation grafted polytrifluorostyrene appears to show some promise as low cost SPE materials. The performance of this material decays with time/24/. The understanding of the performance decay mechanism may result in better membranes.

6.1.2 Electrodes and Current Collectors

Chemical/electrochemical corrosion, structural integrity, catalytic activity, surface area and resistance to fouling are important criteria in selection of a viable electrode structure. In a typical cell, teflon bonded catalysts are pressed onto each face of the SPE by a proprietary procedure to form a composite/25/. Current collectors are required in order to distribute the current throughout the surface area of the electrode. They also provide fluid distribution.

The SPE/electrocatalyst and electrocatalyst/current collector interfaces are major causes of ohmic loss in an SPE cell. This contact resistance results in efficiency losses, particularly at high current densities. Improvements in this are being sought by developing new methods of attaching the catalysts to the membrane surface without a binder/26/.

Cathode

Highly activated platinum black is used as the cathode catalyst, the current catalyst loading being 0.2 mg/cm^2. General Electric is making a significant effort to reduce the noble metal loadings through the use of graphite extenders. Catalyst loadings as low as 0.1 mg/cm^2 have been found feasible. A small performance loss, however, is observed probably due to the contact resistance of the graphite contact.

In an electrolyzer, the bulk of hydrogen is evolved at the catalyst and some atomic hydrogen may be transported to the metallic collector. Thus, hydrogen embrittlement and permeability characteristics of the material of cathode current collector are important. Noble metals have characteristics most suitable for this application but using noble metals is too expensive. Their thin coatings on metals such as Ti are used to improve the behaviour of basic structures.

The generally accepted mechanism in acidic media is the discharge of hydronium ion leading to the formation of adsorbed atomic hydrogen followed by their removal by either recombination or electrochemical desorption as given by the following equation:

$$S + H_3O^+ + \bar{e} \rightarrow S\text{-}H + H_2O\ (\ell)$$

$$2S\text{-}H \rightarrow 2S + H_2\ (g)$$

$$S\text{-}H + H_3O^+ + \bar{e} \rightarrow H_2O\ (\ell) + H_2\ (g)$$

where S refers to the active site on the cathode surface. In analogy with acid solutions, probably the electrochemical discharge of H_3O^+ is fast followed by the rate determining step - recombination/4/. In practical SPE cells, the hydrogen reaction is probably controlled by diffusion of molecular hydrogen away from the electrode surface.

Anode

In acidic environments, as encountered in SPE cells, only noble metals and their alloys are suitable for use as electrocatalysts for O_2 evolution reaction.

General Electric probably uses a mixture of noble metal oxides as electrocatalysts and current loading is approximately 1 mg/cm^2. Work is in progress to develop low cost conductive catalyst extenders to allow lower loading of the noble metal content, for large membrane and electrode assemblies. The current collector is similar to the ones described for cathode.

The oxygen evolution in acid media on oxide covered platinum surfaces is generally accepted to occur through the following intermediate reactions/4/:

$$S + 2H_2O\ (\ell) \rightarrow S\text{-}OH + H_3O^+ + \bar{e}$$

$$2S\text{-}OH \rightarrow S + S\text{-}O + H_2O\ (\ell)$$

$$2S\text{-}O \rightarrow 2S + O_2\ (g)$$

Oxygen evolution from acidic media on other precious metals is also believed to occur with same reaction mechanism on Pt. The primary electron transfer process is found to be the rate determining step at higher current densities.

6.2 Present Status

Under the sponsorship of the US Department of Energy and certain electric and gas utilities, General Electric has been developing SPE electrolyzer for large scale H_2 generation applications. Goals of the present work include an overall efficiency of 90% with a system design capable of achieving in production capital costs of $82/KW.

Single cells have been scaled up to 1 m^2. Smaller cells have been successfully designed and operated at temperatures of up to 150°C, pressures of up to 20000 kPa and differential pressures of up to 3400 kPa.

Demonstration of a 200-500 kW cell utilizing the 0.23 m^2 cell was recently being negotiated for.

6.3 Summary

SPE Electrolyzer technology is the most efficient of the commercially available technologies. However, costs of the Nafion membrane and precious metal catalysts hinder its widespread use. No breakthroughs are expected in the near term that could substantially lower the cost of these materials.

7.0 VAPOUR PHASE ELECTROLYZER USING CERAMIC OXIDE ION CONDUCTORS

High temperature water vapour electrolysis promises to be the most economical and efficient method. In this scheme, the water vapour is converted to hydrogen and oxygen gases at ~1000°C in an electrolyzer cell that uses high temperature solid electrolyte. At these temperatures the electrolysis cell may be operated below the thermoneutral voltage, so that heat energy equal to $T\Delta S$ per mole of water is abstracted from the high temperature ambient. Thus, the use of high temperature electrolysis, is particularly attractive from the standpoint of utilizing external heat sources (eg, solar heat, nuclear heat, or recovered process heat), to energetically aid the splitting of the water molecule. A solid oxide electrolyzer would require only 1 - 1.3 V to drive the electrolyzer at practical hydrogen production rates. This compares with about 2 V required with conventional electrolyzers.

Furthermore, at these temperatures the electrode reactions proceed at reasonable rates with significantly lower overvoltages on low cost electrocatalysts.

The advantages of high temperature electrolysis with respect to overall thermal efficiency are obvious as energy costs contribute about 80% of the overall cost of hydrogen produced in large electrolysis plants.

Steam electrolysis using yttria-stabilized zirconia electrolyte tubes and porous platinum electrodes was first reported in 1966/27/. Two volts at 500 MA/cm^2 were required to dissociate steam containing 50% hydrogen at 1000°C. In 1969, Spacil and Tedman/28,29/ were able to electrolyze steam containing 50 mol% hydrogen at 1000°C, at approximately 1.3 V at 500 mA/cm^2. Interest in solid oxide electrolyzers has been growing since then. A sizeable research effort in developing this technology is now being directed in West Germany (Dornier Systems) and the US (Westinghouse).

7.1 Components of a Solid Oxide Electrolyzer

A solid oxide water electrolyzer consists of a thin ceramic membrane coated with porous anode and cathode on the two sides, as shown in Figure 9. Water vapours to be electrolyzed are introduced to the cathodic compartment. When voltage is applied across the anode and cathode, the following reaction takes place at the cathode.

$$H_2O + 2\bar{e} \rightarrow O^{2-} + H_2 \qquad (14)$$

The oxide ion is transported to the anode through the solid electrolyte via lattice defects. At the anode, it is discharged as O_2 according to the reaction

$$O^{2-} \rightarrow 2\bar{e} + \tfrac{1}{2} O_2 \qquad (15)$$

Most of the present high temperature electrolyzer programs rely on ceramic oxygen ion conductors such as yttrium and zirconium oxides (28-39). Due to the rather small conductivity of these electrolytes at low temperatures, the cells must be operated at 1000°C in order to obtain reasonable hydrogen production rates. This high temperature operation presents a severe problem of finding the right sealant, electrode and interconnection materials with acceptable electrical, chemical, thermal and stress behaviour. Two approaches have been tried to lower the operating temperature and hence alleviate this problem.

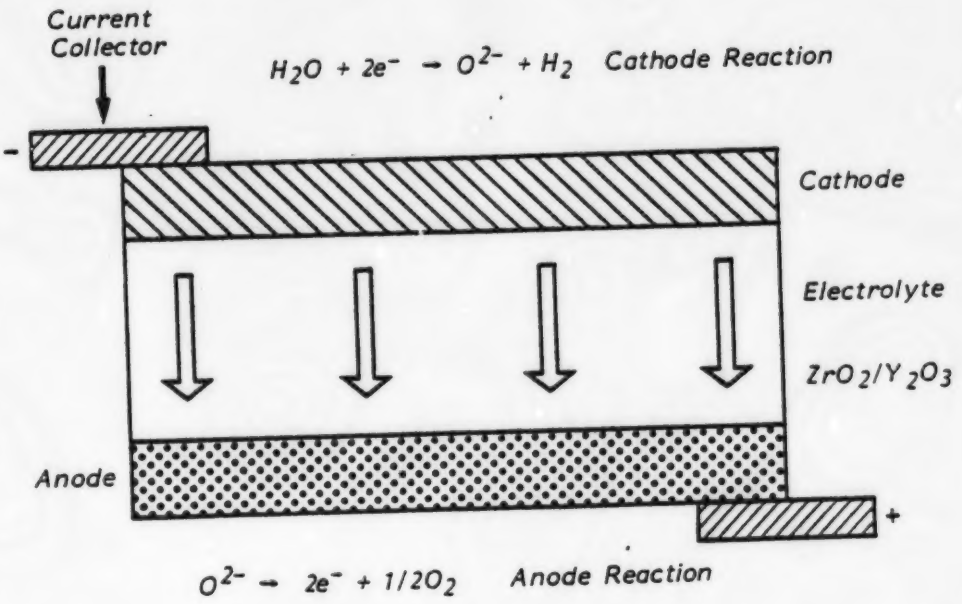


FIGURE 9

SCHEMATIC DIAGRAM OF A SINGLE CELL OF A SOLID OXIDE WATER VAPOUR ELECTROLYSER. /2/

1. A number of new solid oxide anionic conductors have been investigated. The new electrolyte should have high anionic conductivity (and very low electronic conductivity) at operating temperatures under highly reducing as well as oxidizing atmospheres/31/. Furthermore, it should be impervious to gases. The electrolyte properties should remain unaltered during long-term operation. No one material has been found that meets all the above requirements and also has a high thermal shock resistance. It is likely, that some breakthroughs may occur in this area. Alternatively, it is possible that hydrogen ion conductors may replace the oxide in conductors as discussed later.

2. Thinner membranes have been developed to minimize the ohmic losses in the cell. Pioneering work in this direction has been conducted by Dornier Systems in West Germany under the HOT ELLY Project/32-33/. Electrolyte and electrode structures of the order of 100 μm thick have been assembled on supporting ceramic materials/2/. More recently Westinghouse has also come out with similar cell designs.

7.2 Single Cell Design

As the smallest unit of the electrolyzer, single cells can be either flat or cylindrical shaped. The hollow cylinder is mechanically more stable than the flat membrane. The sealing length between anode and cathode compartment is larger for the flat design. This is a serious disadvantage of the planar geometry. As a result all tests have been limited to tubular single cells only.

7.3 Scale Up and Multiple Cells

For increasing the hydrogen output of an electrolysis unit, the active area of the electrolyzer has to be enlarged. This cannot be achieved by simply increasing the single cell dimensions, because ceramic fabrication technology is more suitable for small parts than for larger ones. In addition:

i) Most ceramic parts have low tensile strength and no ductility.

ii) Mechanically stable and gas tight high temperature joining of ceramics is difficult, therefore, the total length of interconnection has to be as small as possible.

iii) Current collecting electrodes have a relatively low electrical conductivity. Therefore, in order to avoid high ohmic losses, the current density within the electrode has to be kept low.

Serial connection of single cylindrical cells is the preferred configuration. Figure 10/33/ shows a multicell electrolyzer developed under Doniers Hot Elly Project. Tubes of the electrolyte are interconnected by gas-tight rings of an electronically conducting material. By its design, the electrical serial connection and gas tight separation of anode and cathode gas space could be realized very easily.

Stacks of serially connected cells can be built up from electrolyte tubes and rings of the interconnecting material by a diffusion welding process and subsequent spraying of electrodes. At 1000°C, the tubes can stand pressures of eight bars at ambient pressures outside/33/. Over long operating periods, the electrical behaviour of multicell stacks has been demonstrated to be very stable. The performance of a unit cell of such an electrolysis tube is shown in Figure 11. Current efficiency was 100% over an 800 hour period and no degradation of performance could be detected during the whole experiment/33/.

As an extension of the fuel cell program, Westinghouse has revitalized its solid oxide electrolyzer program. The electrolyzer consists of a porous zirconia tube onto which electrolyte and electrodes are deposited using proprietary techniques. Interconnection to the inner electrode is provided using a series of fabrication steps in which the interconnection part of the inner electrode is masked while the electrolyte and the outer electrode coatings are being employed. Nickel sponge is used to interconnect different cells in series and parallel arrangement.

At Westinghouse/27/, electrochemical cells employing yttria stabilized zirconia solid electrolyte have been evaluated in the electrolysis of steam at 800 - 1050°C. Performance levels of 1.23 V at 300 MA/cm^2 were obtained with current efficiencies approximating 100%. A limiting current was approached when the hydrogen content in steam exceeded 90% (650 MA/cm^2 at 100°C). Voltage-current behaviour prior to diffusion control follows a Tafel type slope of approximately 250 MV/decade.

The concept of coupling fusion power plants with solid oxide electrolyzers has been examined at Brookhaven National Laboratory/4/. A conceptual design of the system is shown in Figure 12. Heat produced in the fusion reactor blanket is supplied to the endothermic water vapour electrolyzer and to the power conversion unit where the electricity for the electrolyzer is produced. The number of electrolyzers is a function of blanket temperature, the temperature change within each electrolyzer, the outlet hydrogen concentration and the upper temperature limits of the conventional steam generators.

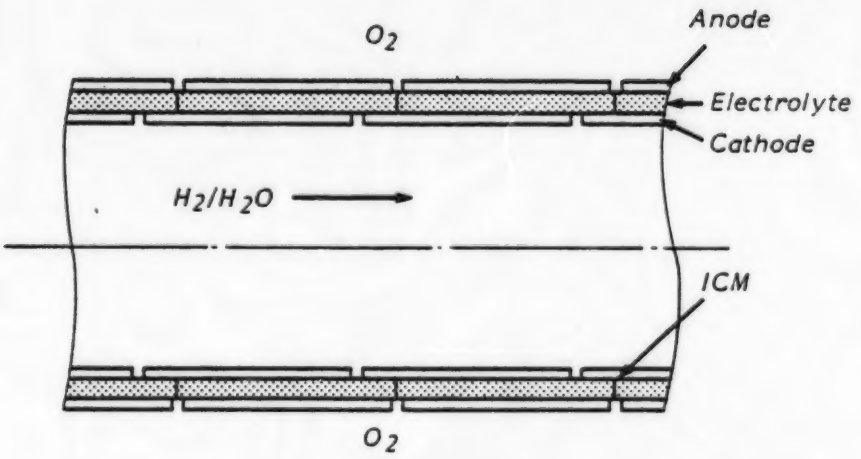


FIGURE 10

SERIAL CONNECTION OF CYLINDRICAL SINGLE CELLS
THE ELECTROLYTE TUBES ARE JOINED BY
GAS-TIGHT RINGS OF INTERCONNECTING MATERIAL (ICM) /33/

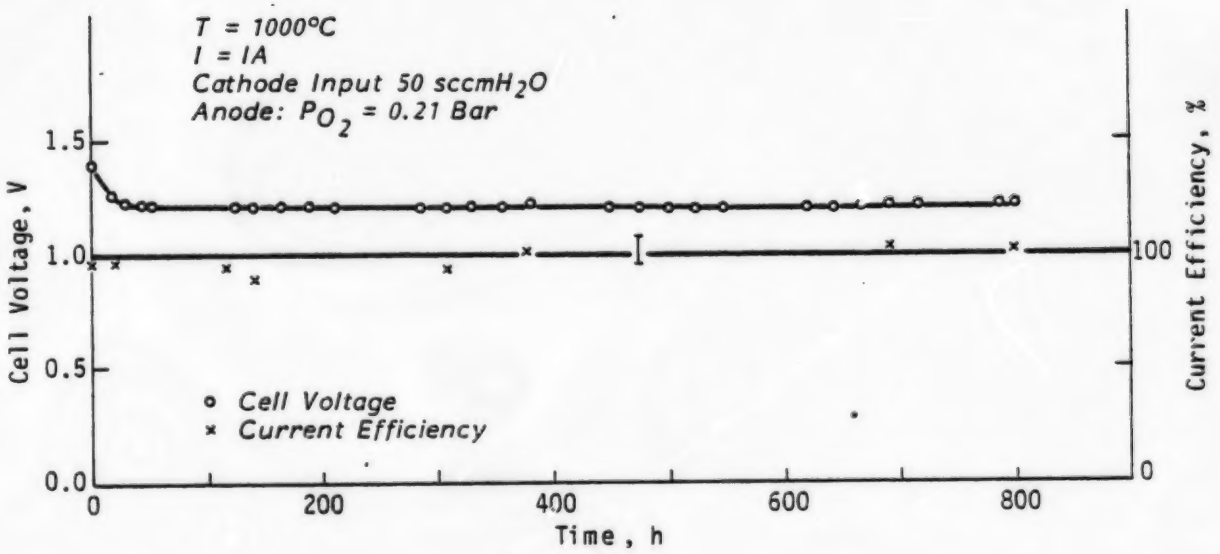


FIGURE 11

MEAN CELL VOLTAGE OF AN ASSEMBLED STACK OF CELLS INCLUDING INTERCONNECTION LOSSES. THE CURRENT EFFICIENCY IS 100% OVER THE WHOLE TEST RUN./33/

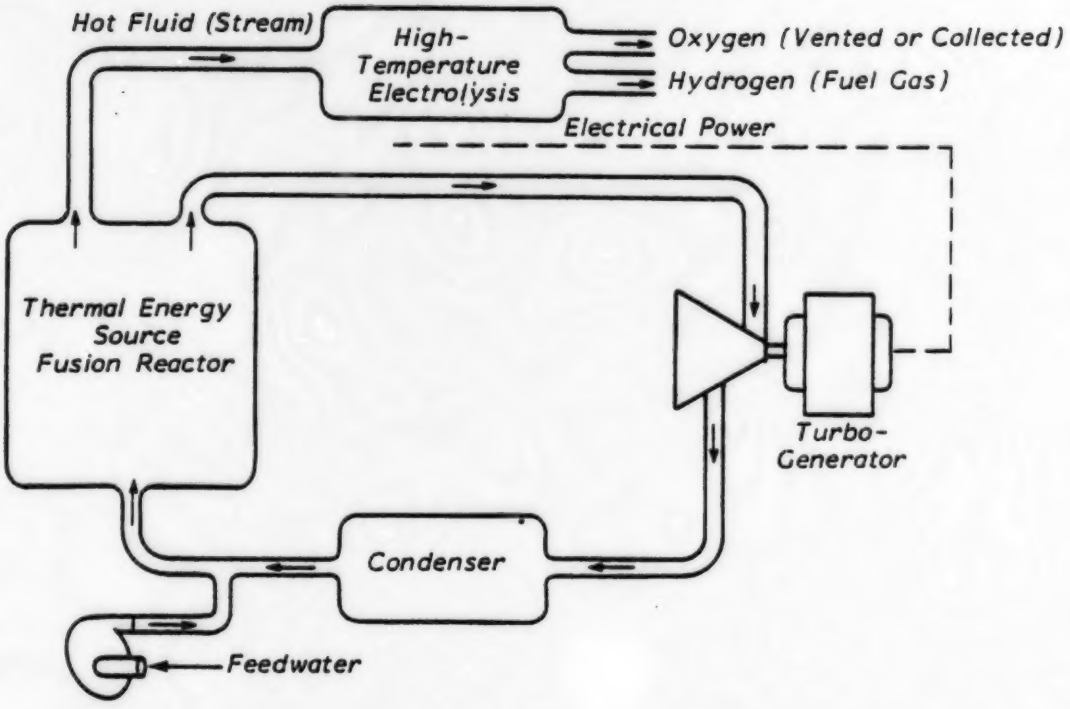


FIGURE 12

CONCEPT OF FUSION REACTOR COUPLED WITH SOLID ELECTROLYTE WATER ELECTROLYZER-GENERAL HTE PROCESS WITH CONVENTIONAL POWER CYCLE /4/

Another interesting configuration of high temperature water vapor electrolyzer may use fuel gases in the anodic compartment/28/. The anode reaction in this case becomes

$$O^{2-} + \text{Fuel} \rightarrow \text{Oxidized Fuel} + 2\bar{e} \qquad (16)$$

The low potential of the fuel electrode in this type of cell will reduce the cell voltage compared to an oxygen anode cell and can thus reduce the energy required for the dissociation of water.

7.4 Decomposition of Tritiated Water With Solid Oxide Electrolyzer

A vapour phase electrolyzer based on this technology has been proposed for the decomposition of tritiated water in tritium and fusion applications. The cell requires a very low tritium inventory. Its components are not subject to radiation damage and no solid wastes are produced. A 50 cm^2 electrode area cell based upon yttria stabilized zirconia, developed by Dr. S. Konishi of the Japan Atomic Energy Research Institute, is currently being tested at the Tritium System Test Assembly at the Los Alamos National Laboratory, Los Alamos.

8.0 VAPOUR PHASE ELECTROLYZERS USING SOLID PROTON CONDUCTING ELECTROLYTES

High temperature operation of electrolyzers offers an attractive route for avoiding activation overpotentials and utilizing high temperature waste heat from various sources. Most conceivable solid oxide electrolyzers can achieve this but they require a source of very high temperature waste heat (600-1000°C) and the material problems at these temperatures are immense. It would be ideal if an electrolyte can be found with acceptable conductivity in the 100-300°C range so that the material problems are manageable and CANDU waste heat can be utilized. No solid oxide electrolyte has been found that will have acceptable conductivity in this temperature range.

A new class of proton conducting solid state materials has been identified during the last decade. Some of these materials have large concentrations of mobile protons and vacant sites with a small hopping energy between an occupied and vacant level. As a result they demonstrate high proton conductivities. The interest in these materials is growing because of their prospectus in fuel cells, water electrolyzers, batteries, hydrogen monitors, electromagnetic displays and capacitors.

For application in water electrolysis (and fuel cells), proton conducting electrolytes should meet the following requirements:

- good chemical and thermal stability up to ~300°C.
- high ionic conductivity (0.1 Ω^{-1} cm^{-1})
- ease of manufacture in suitable shapes and sizes.

Table VII/34/ lists different solid state ceramic proton conductors that have been investigated. As can be seen, most of these materials are unstable above about 100°C, losing water content and proton conductivity. The existence of H_3O^+ - β^{11} alumina with good thermal stability provides hope that other hydrated compounds may be found that are capable of supporting fast proton conduction and hold their water to medium temperatures (~300°C).

A number of organizations are involved in developing or evaluating H_3O^+ - β^{11} alumina/17/. New materials comparable to or better than H_3O^+ - β^{11} alumina are also being developed. The Canadian program, funded by NRC under the project leadership of Dr. M. Hammerli and conducted jointly by Prof. M. Sayer (Queens University, Kingston) and Prof. P. Nicholson (McMaster University, Hamilton) appears significantly ahead of other programs. Because of the importance of this program to Ontario Hydro, a somewhat detailed account is given below, although the program is still in the early stages of development.

8.1 Canadian Program on Proton Conductors

The Canadian program is aimed at finding new electrolytes with acceptable conductivities at 200-400°C/2/, so that heat at the CANDU reactor outlet temperature can be utilized to decrease the electricity requirements in water electrolysis. Needless to say, in this temperature range the material problems will be manageable.

As part of Canada's contribution to the International Energy Agency's Hydrogen Programs, a review was conducted to identify hydrogen ion conductors. β^{11} - alumina (0.84 H_2O·0.84 MgO·5 Al_2O_3·2.8 H_2O) was identified as being the most promising material/2/. Most investigations using hydronium β^{11} alumina have, however, been limited to the material in single crystal forms. It has been difficult to manufacture this compound in a commercially viable ceramic form since it decomposes well below the sintering temperature. Following the recommendation of this study a two phase major program was started to:

- develop new proton conductors with characteristics comparable with β^{11} alumina.
- develop new routes to the fabrication of hydronium β^{11} alumina.

TABLE VII/34/

FAST PROTON CONDUCTORS

Compounds	Temperature Limit of Possible Use [°C]	E_A [eV]	σ_{RT} $[(\Omega cm)^{-1}]$
ZrO_2, nH_2O	-	0.3	10^{-5}
SnO_2, nH_2O	40	0.2	10^{-4}
$H_2Sb_4O_{11}, 3.1H_2O$	20	0.4	10^{-3}
$H_2Sb_4O_{11}, 2.15H_2O$	80	0.7	10^{-7}
$\alpha Zr(HPO_4)_2 . 2H_2O$	-	-	10^{-2} 10^{-9}[a]
alunite $(H_3O^+)Al_3(SO_4)_2(OH)_6$	60	-	10^{-4} 10^{-9}[a]
micas			
HUP	60	0.3	4.10^{-3}
HUAS	-	0.2	-
clays			
Montmorillonite	-	-	-
$\gamma AlOOH$	-	-	10^{-6}
zeolites			
natrolite: $NO_2Al_2SiO_{10}, 2H_2O$	200	-	10^{-4}-10^{-9}[a]
mordenite: $H_{4.3}(NH_4)_{4.4}$			
$(AlO_2)_{8.7}(SiO_2)_{39.3}$	200	-	10^{-3}-10^{-7}[a]
$H^+(H_2O)_n$ β/β^{11} Al_2O_3	200	0.20	10^{-5}
$H^+(NH_3, H_2O)_n \beta/\beta^{11}$ Al_2O_3	200	0.20	10^{-5}
NH^+_4 β Al_2O_3	350	0.5	10^{-6}

[a]The actual value depends on the partial pressure of H_2O.

Major breakthroughs have been made in both directions:

- New proton conducting ceramics/17/ based on silicate structure (sodium gadolinium silicate and sodium yttrium silicate) have been developed with proton conductivities comparable with or better than the aluminas at the same temperature. These materials have advantages in that they are three dimensional conductors as compared to the two dimensional aluminas. Further development and evaluation of these proprietary materials is in progress.

- During efforts to develop fabrication techniques for $H_3O^+ - \beta^{11}$ alumina, a new proprietary solid proton conductor based on β^{11} alumina structure and exhibiting high conductivity was developed/35/.

Since $H_3O^+ - \beta^{11}$ alumina cannot be sintered directly, it is necessary to prepare alkali ion or mixed alkali ion compositions and sinter them to the required forms. The hydronium analogue may then be formed by ion exchange techniques. Although pure sodium β^{11} alumina can readily be sintered into single phase ceramics with high density, the lattice expansion on H_3O^+ ion exchange leads to mechanical degradation. Based on unit cell dimension considerations, K^+ analogue should be a more appropriate starting material. However, $K^+ - \beta^{11}$ alumina converts readily to $K^+\beta$ alumina during sintering.

Recent work at Queens and McMaster Universities has shown that certain mixed alkali ion composites containing a fraction of alumina in β-phase are suitable for producing proton conducting ceramics/35/. Field assisted hydronium ion exchange of the mixed alkali metal ion analogues can be conducted in an electrochemical cell. A proprietary material prepared in this manner has shown conductivity of 6×10^{-6} ohm^{-1} cm^{-1}, a value consistent with literature values for single crystal hydronium β^{11} alumina. The conductivity of this material obeys the Arrhenius equation with an activation energy of 0.56 eV. It is projected to have conductivities as high as 0.1 Ω^{-1} cm^{-1} at 300°C. Further work on production procedures and optimization is in progress.

The above material is a promising candidate for use in medium temperature (100-350°C) fuel cells and water electrolyzers. A 1 cm^2 single electrolysis cell employing disc shaped hydronium electrolyte and porous platinum electrodes has been operated for over 1000 hrs/35/. Another unit is being constructed to operate at higher temperature (up to 350°C).

Provided conductivities as high as projected can be obtained and the material stands its promise of chemical and thermal

stability at 300-350°C, it may find a number of applications of interest to Ontario Hydro.

- A water vapour electrolyzer operating at 100-300°C may utilize CANDU waste heat as well as electricity to produce hydrogen.

- Vapour phase electrolyzers may be used to decompose tritiated water. Such electrolyzers will have all metallic and ceramic components so that there will be no tritiated waste disposal problems. Tritium inventory requirements for such a cell are minimum and material and permeation problems are significantly lower than the other electrolyzer using oxide ion conducting electrolytes.

- Hydrogen concentrators can be used to selectively recover hydrogen (and its isotopes) from other gases with all the advantages sited for vapour phase electrolyzers.

- In early stages of operation as tritium concentrators, these materials, act as tritium getters so that they have a potential application in tritium gettering.

- The electrolyzer is reversible so that it can be used in the fuel cell mode minimizing activation overpotential losses.

As is evident, these materials have potential application not only in the utilization of CANDU electricity and heat but also in tritium removal and handling. It is prudent that OHRD monitor the developments at Queens and McMaster and where possible encourage the work on applications.

Due to the newness of the technology, some fundamental questions also remain to be answered. The Danish-French Workshop on "Solid State Materials for Low to Medium Temperature Fuel Cells and Monitors, with special emphasis on Proton Conductors", held in Paris, December 1981/36/ concluded with the following remarks on proton conductors:

- The transport mechanism in solid proton electrolytes remains controversial because of a lack of adequate characterization of the way the water molecules are incorporated into the solid.

- The conduction of protons as oxonium ions and the associated back diffusion of water should be considered in the study of proton conducting materials.

- High water vapour pressure exhibited by most of the presently known protonium conductors poses an important problem. Any instability of the electrolyte to a variation in water vapour pressure must be suppressed.

- There are some cases where proton conductivity may be maintained at low vapour pressure. A promising example was identified as the materials with zeolite structure in which water is strongly adsorbed over a large internal surface.

9.0 NOVEL ELECTROCHEMICAL PROCESSES FOR HYDROGEN GENERATION

9.1 Photoelectrolysis of Water

In 1970 Fujishima and Honda/37/, using illuminated n-type semiconducting TiO_2 anodes, showed that decomposition of water could be achieved at a significantly lower applied potential compared to the thermodynamically required 1.23 V. During this process, now known as photoelectrolysis, optical energy is converted into chemical energy in the form of free energy of the resultant products. International research and development effort in this new area has been growing rapidly.

The simplest form of the cell consists of two electrodes immersed in an aqueous electrolyte and connected electrically by a wire. One of these electrodes is a metal that does not react chemically with the electrolyte: the other electrode is a semi-conductor with one face in contact with the electrolyte and the other face connected to the shorting wire by an ohmic contact. Ideally, when light falls on the semiconductor electrode, oxygen gas is liberated at one electrode and hydrogen is liberated at the other. (Oxygen is liberated at the semiconductor if it is n-type, hydrogen if it is p-type).

The operation of such a cell can generally be explained in terms of electron energy levels in the electrodes and the electrolyte. The semi-conductor is characterized by a filled valence band and a nearly empty conduction band separated by a forbidden band. Between these lie the Fermi level, which is equivalent to the chemical potential for electrons in the semiconductor. Its position in the gap depends on the presence of impurities in the semiconductor that "dope" it to provide charge carriers for n-type semiconductor, electron donors provide electrons in the conduction band; for p-type, acceptors produce "holes" in the valence band. The Fermi level is generally close to the band with the preponderence of charge carriers.

Similarly, energy levels in an electrolyte are determined by the solvent and the ionic species within it. In an aqueous electrolyte with one mole of H^+ (or H_3O^+) ions per liter of water (pH = 0) the energy of the Fermi level of a metal electrode that can just contribute electrons to the reaction $2H^+ + 2e \rightarrow H_2$ is 4.5 electron volts (eV) below the vacuum level for electrons outside the electrolyte. As the concentration of H^+ decreases, the Fermi energy of the electrode in the hydrogen evolution reaction increases (approaches the vacuum level) by 0.059 eV per decade decrease in H^+ concentration, in accordance with the Nernst equation. Thus, at pH = 7 (10^{-7} moles of H^+ per litre), the electrode potential for H_2 evolution (or more simply the hydrogen potential) would be -0.41 volts relative to the potential of a NHE.

The minimum thermodynamic free energy to cause the water splitting reaction $H_2O \rightarrow H_2 + 1/2\ O_2$ at standard temperature and pressure is 2.46 eV per water molecule (56.7 kcal $mole^{-1}$) or 1.23 eV per electron transfer. Thus, the Fermi level of a metal electrode that will accept an electron in the reaction $H_2O \rightarrow 2H^+ + 2\bar{e} + 1/2O_2$ must be at least 1.23 V positive with respect to the hydrogen potential. To get a finite current flow across the electrode-electrolyte interface the electrode must be more than 1.23 volts positive.

The relationship of the semiconductor bands to the energy levels of the electrolyte can be determined by measuring the so-called flat-band voltage. When a voltage equal to the flat band potential is applied to the semiconductor there is no electric field internal to the semiconductor, and so the energy levels in the bulk are the same as they are at the surface. When the voltage applied to the semiconductor is not at this special value, its charge adjusts itself, resulting in an electric field manifested by the bending of the bands near the surface to connect the band levels in the bulk to the band edges at the surface. In the usual case of reverse bias (n-type more positive or p-type more negative than the flat-band potential), this surface potential change results in the draining of majority carriers from the surface to the bulk of the semiconductor, thus creating a depletion region. In n-type semiconductors this means that the bands bend up toward the surface; in p-type materials the bands bend downward. In the absence of large current densities across the interface, the potential adjustment occurs in the semiconductor depletion region, which becomes virtually equivalent to an insulator, while the electrolyte for cases of practical interest has a much higher conductivity. Thus, in reverse bias the energies of the semiconductor bands at the interface remain fixed relative to the energy levels in the electrolyte.

Figure 13 illustrates typical band configurations in reverse bias for both types of semiconductors in contact with an electrolyte that is assumed to be acid. When the semiconductor is irradiated with photons having sufficient energy to raise an electron from the valence band to the conduction band it creates a mobile hole in the valence band and a mobile electron in the conduction band. The extra majority carrier represents very little change in the semiconductor; but the extra minority carrier represents an important change. Most of the free energy due to illumination is associated with these minority carriers/38/.

If the photon energy is greater than the bandgap energy, the excess energy is quickly thermalized within the semiconductor so that the holes are at the top of the valence band and the electrons are at the bottom of the conduction band. The energy stored by the interband transition is then just of the band gap. The existence of the gap prevents the immediate recombination of the electrons and holes and makes it possible to use the stored energy. The electric field in the depletion regions shown in Figure 13 acts to separate the oppositely charged photo-excited carriers, decreasing the majority carrier density and increasing the minority carrier density at the electrode surface. This separation of charge by the band bending is one of the key features that make semiconductor photoelectrochemistry so attractive. The electrons and holes are prevented from recombining at the surface and the free energy of the minority carriers is delivered to the surface where it can drive chemical reactions.

Figure 14 indicates some of the transitions possible at the surface of an n-type semiconductor anode. An electron at a very high energy in the electrolyte, marked by E° in Figure 14a may enter the conduction band of the semiconductor; but its transfer to a hole in the valence band is extremely unlikely. If the redox level lies in the middle of the bandgap (Figure 14b) the electron cannot transfer from the electrolyte to the conduction band and is unlikely to pass directly to a hole in the valence band. If an appropriate surface state is present, however, the electron can tunnel to the surface state, and once in the surface can combine with the hole.

When the redox level is closer to the valence band edge but still above it, the probability of a direct transfer is greatly increased (Figure 14c). Once the redox level is below the valence band edge (Figure 14d) the electron cannot enter the semiconductor, but an oxidized state at this level could inject a hole into the valence band by withdrawing an electron from it. Similar considerations govern the passage of electrons between an electrolyte and p-type semiconductors.

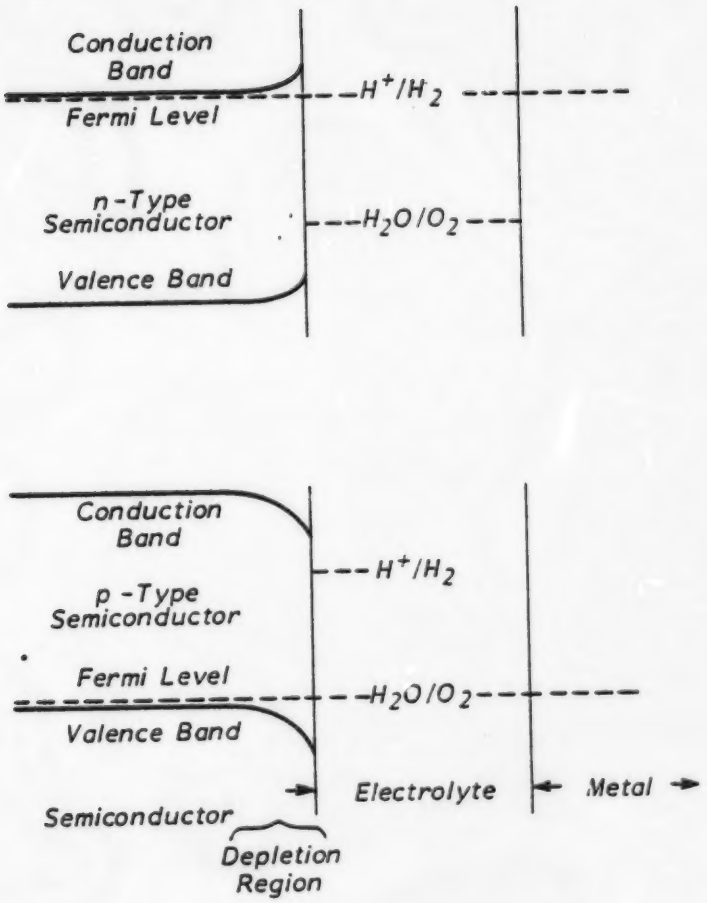


FIGURE 13

SCHEMATIC ILLUSTRATION OF THE RELATIVE ENERGY LEVELS OF PHOTOELECTROCHEMICAL CELLS SPLITTING WATER WITH NO EXTERNAL VOLTAGE AND NO OVERVOLTAGE/38/

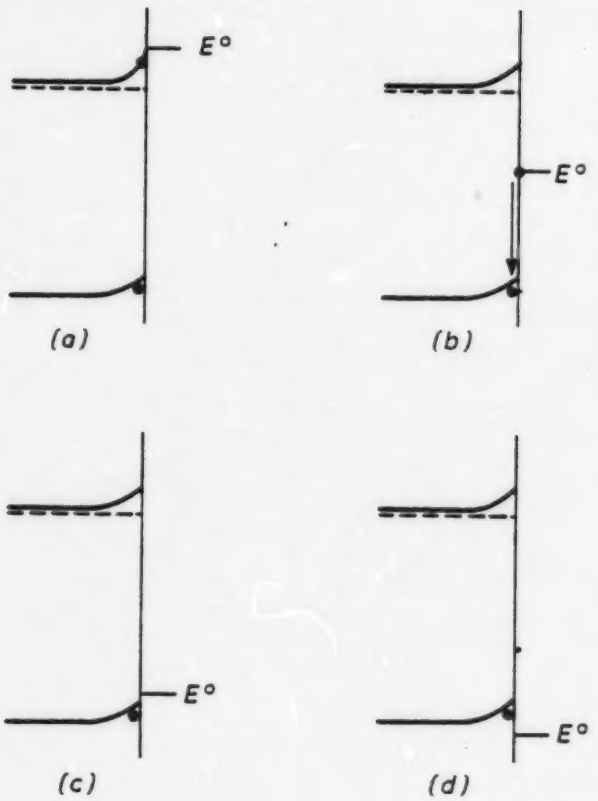


FIGURE 14

SCHEMATIC ILLUSTRATION OF REDOX ENERGIES, E°, RELATIVE TO THE BANDS OF A SEMICONDUCTOR ELECTRODE.
(a) E° ABOVE THE CONDUCTION BAND ALLOWING ELECTRON TRANSFER TO THE CONDUCTION BAND;
(b) E° AT MIDDLE OF THE BAND WHERE ELECTRON TRANSFER TO PHOTOEXCITED HOLES IN THE VALENCE BAND IS THROUGH SURFACE STATES;
(c) E° NEAR THE VALENCE BAND WHERE DIRECT ELECTRON TRANSFER TO PHOTOEXCITED HOLES IS POSSIBLE;
(d) E° BELOW THE VALENCE BAND SO THAT NO ELECTRON TRANSFER TO THE SEMICONDUCTOR IS POSSIBLE.
DISTRIBUTIONS OF ION ENERGIES ABOUT THE REDOX ENERGY ARE NEGLECTED FOR SIMPLICITY/38/.

Semiconductor Requirements to Decompose Water

For an n-type semiconductor the counter electrode is at the potential for hydrogen evolution, and for p-type, at the oxygen evolution potential. When the electrodes are shorted to each other, the Fermi level of the semiconductor is at the same energy as the Fermi level of the counter electrode. Thus, the Fermi level of an n-type semiconductor should be enough above the hydrogen evolution potential to get sufficient reverse-bias band bending to prevent electron-hole recombination plus an allowance for overvoltage at the counter electrode and voltage drops in the electrolyte. For a p-type semiconductor, the Fermi level should be below the oxygen evolution potential by a corresponding amount. Failure to meet this requirement can be compensated by an externally applied voltage at the expense of externally supplied energy. As long as this external voltage is less than 1.23 volts, there is a net energy gain from the photons. Thus to split water without an external voltage the bandgap energy of the semiconductor electrode must exceed about 1.5 eV, and its band edge must be suitably placed with respect to the oxygen and hydrogen evolution potentials.

There is a practical upper limit, however, on the size of the bandgap if it is to be an effective absorber of sunlight. The semiconductor's bandgap must be consistent with the distribution of energy in the solar spectrum at the earth's surface. Figure 15 shows this distribution for three kinds of sunlight: that measured outside the earth's atmosphere (termed AM 0 or air-mass 0), that which has passed through an equivalent of two thicknesses of clear atmosphere (AM 2), and that which arrives so obliquely that it passes through five effective thicknesses of atmosphere (AM 5). Figure 16 shows that the collection efficiency can reach as high as 50% for a band gap of 1.1 eV, but this is too small a gap to decompose water. Not all the energy absorbed in the semiconductor is usefully stored as hydrogen, even if every photon absorbed is ultimately responsible for producing one hydrogen atom. The stored energy in each hydrogen atom is 1.23 eV, regardless of how much greater the bandgap energy or the photon energy is. Taking this factor into account, the portion of radiant energy effectively stored as H_2 can be calculated. These considerations show that the useful range of bandgaps is quite severely limited to those between say 1.5 and 2.5 eV, small enough to match the solar spectrum, but wide enough to decompose water effectively. Unfortunately, most semiconductors in this range corrode readily when incorporated in an aqueous photoelectrochemical cell.

Several approaches to overcoming the corrosion problem have been proposed. Since small bandgap semiconductors can efficiently absorb solar energy but some wide bandgap materials are more

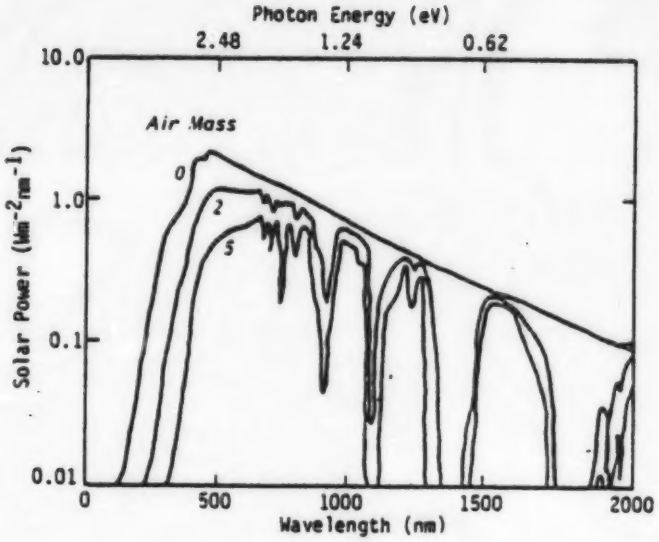


FIGURE 15

DISTRIBUTION OF ENERGY IN THE SOLAR SPECTRUM FOR: AIR MASS 0, JUST OUTSIDE THE EARTH'S ATMOSPHERE; AIR MASS 2, AFTER TRANSVERSING TWO THICKNESSES OF CLEAR ATMOSPHERE (ABOUT 60° FROM VERTICAL); AIR MASS 5, AFTER TRANSVERSING FIVE THICKNESSES OF CLEAR ATMOSPHERE/38/.

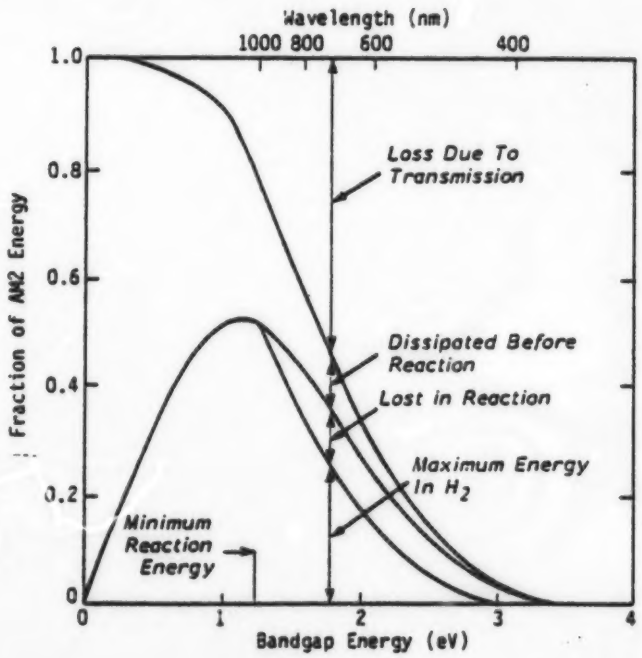


FIGURE 16

DISTRIBUTION OF ENERGY LOSSES IN THE CONVERSION OF SOLAR ENERGY TO HYDROGEN ENERGY FOR SEMICONDUCTOR ELECTRODES AS A FUNCTION OF THE SEMICONDUCTOR BANDGAP ENERGY/38/.

stable, it has been proposed that a thin coating of wide-gap material could protect the more desirable small bandgap material/38/. A more successful approach has been to introduce species in the electrolyte that provide reaction to compete with the corrosion reactions.

Oxide Semiconductors for Photoelectrolysis of Water

The photoelectrochemical behaviour of a number of semiconductor metal oxides/38-40/ and mixed metal oxides/38/ has been studied for application to hydrogen generation. Some of them are shown in Figure 17.

A feature of oxide semiconductors that makes them attractive as photoelectrodes is the possibility of making them in large areas by very simple and inexpensive processes such as electrochemical oxidation, chemical vapour decomposition and sputtering. These inexpensive fabrication techniques yield electrodes that behave similar to single crystal electrodes in many respects. Their bandgaps and band-edge positions are the same but they differ from single crystals in effective diffusion length. The polycrystalline nature of the film materials implies a higher degree of disorder with a large density of scattering and recombination centers within the bulk. As a consequence, the quantum efficiency tends to be lower, and the well-defined current onsets and saturation currents characteristic of good single-crystal electrodes tend to be more gradual and lower in value. If the need for external voltage with one of these narrower-bandgap oxides could be eliminated and this inexpensive formation process optimized, then economical photoelectrochemical hydrogen production would be feasible.

The valence bands of these oxides are generally attributed to the oxygen anion, while the conduction band is associated with states of the metal cation. The valence bands of most oxide semiconductors tend to occur at the same absolute level. The trend in both band-edge positions is shown in Figure 17. It shows that both band-edges shift as the bandgap decreases, with the decrease in the energy level of the conduction band being somewhat greater than the increase in the valence band level. Thus, narrower-bandgap semiconducting oxides have lower flat-band energies and require more external bias to make them decompose water photoelectrochemically. Certainly, it is true that only the widest bandgap materials, $KTaO_3$, $SrTiO_3$, and $CaTiO_3$ have flat bands high enough to operate without bias, but SnO_2 seems to be an exception to this rule, and there is some disagreement regarding the behaviour of $BaTiO_3$. It appears that all of these materials exhibit the expected shift of 59 mV/pH unit as the pH of the electrolyte is varied. This behaviour implies that the positions of the flat-band voltages remain

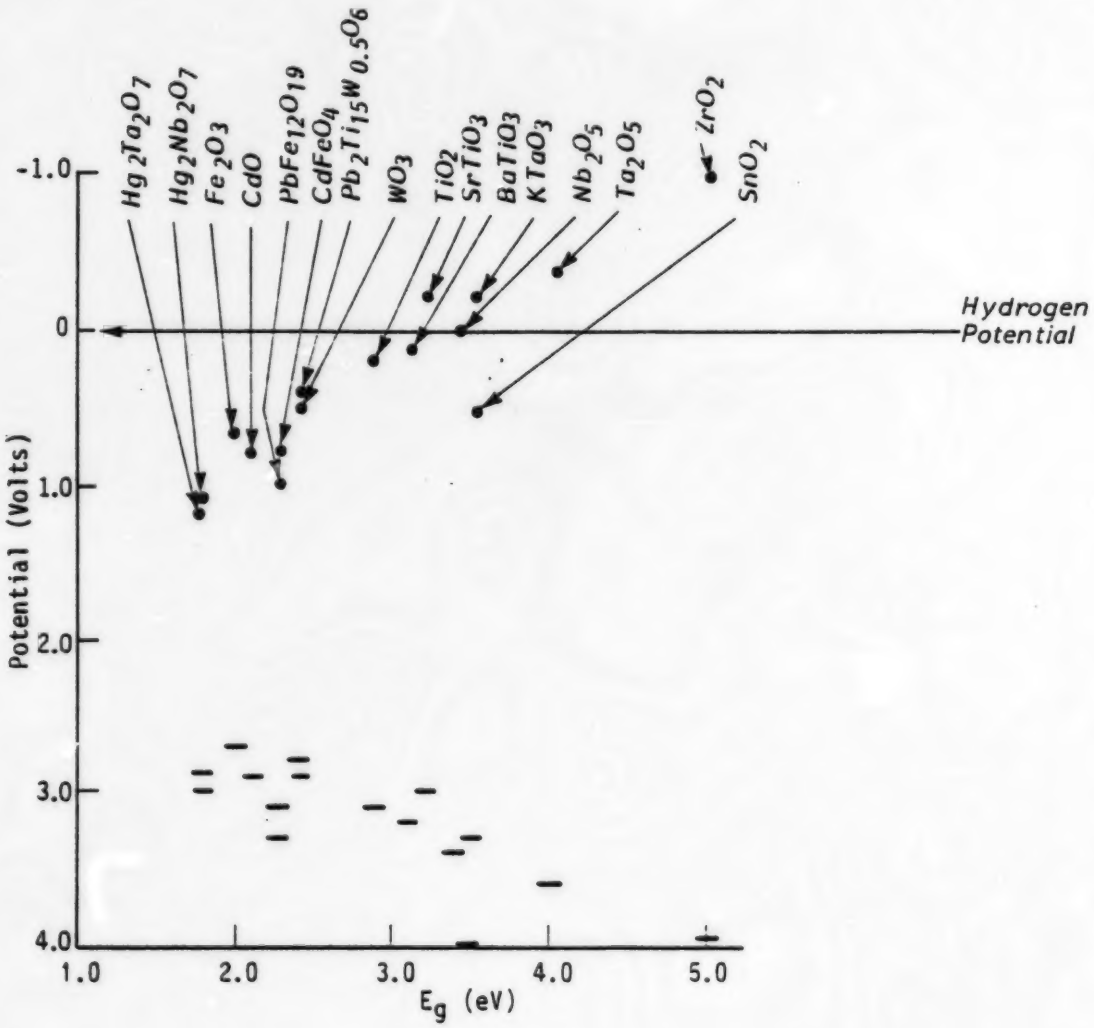


FIGURE 17

PLOT OF POTENTIAL FOR PHOTOCURRENT ONSET FOR SEVERAL OXIDE SEMICONDUCTORS AT pH=13.3vs THE BANDGAP OF THE SEMICONDUCTOR, THESE POTENTIALS APPROXIMATE THE POSITIONS OF THE CONDUCTION BAND FOR n-TYPE SEMICONDUCTORS. THE BARS (-) CORRESPOND TO THE APPROXIMATE POSITION OF VALENCE BANDS/38/.

fixed relative to the water decomposition reactions, H^+/H_2 and OH^-/O_2, which shift with pH in the same way.

In a conventional photoelectrolysis cell, one of the electrodes must be illuminated with light. Scaling up of such a device is likely to be difficult and/or costly. Neither the bipolar stacking of individual cells nor the unipolar tank configuration of conventional water electrolyzers is appropriate here/2/.

The concept of photochemical diode for hydrogen production has evolved as an extension of photoelectrolysis cells/2/. In a photochemical diode, the p- and n-type electrodes are in direct ohmic contact with each other. The diodes can, in principle, be fabricated in very small sizes. The photocatalytic powder of this kind can be slurried in water. Since no external voltage is required to dissociate water, H_2 and O_2 could be produced directly from sunlight. Photocatalytic powders have been used to synthesize a number of other products such as H_2O_2 from O_2 and ammonia from N_2/41/.

9.2 Electrolyzer Using Anodic Depolarizers

In a conventional water electrolyzer the oxygen overpotential at the anode contributes significantly to its inefficiency. Attempts are being made to diminish the oxygen overpotential by developing new electrocatalysts or by operating the electrolyzers at elevated temperatures. Using new electrocatalysts, it will be difficult to reduce the cell potential, for production of hydrogen from water, below 1.3 V. It has been shown that the cell potential can be reduced by replacing the anodic reaction by other reactions such as carbon or SO_2 oxidation. The material needed for an alternative anodic reaction should possess the following characteristics:

- It should be cheap, so that the reduction in the cost of hydrogen is greater than the cost of the depolarizer.
- The product at anode should preferably have a commercial value. Alternatively, it must not be noxious and should be easy to remove.

Coal as Anodic Depolarizer

In principle, a coal slurry may be used to depolarize the anode of a water electrolysis cell according to:

At anode

$$C(s) + 2H_2O(l) \rightarrow CO_2\ (g) + 4H^+ + 4\bar{e}$$

at cathode

$$4H^+ + 4\bar{e} \rightarrow 2H_2\ (g)$$

where s, l, and g denote the solid, liquid and gaseous phases respectively. The net reaction is the electrochemical gasification of coal.

$$C(s) + 2H_2O\ (l) \rightarrow 2H_2\ (g) + CO_2\ (g)$$

Theoretical reversible potential for the above reaction is 0.21 V, which is only 17% of the 1.23 required for water electrolysis/2/. The consumption of coal is thus, responsible for this much smaller theoretical cell voltage.

Coughlin and Farooque/42-43/ were the first to demonstrate the use of coal as an anodic depolarizer. They found that the current efficiency for CO_2 formation at the anode is 25-50%. Much higher current efficiencies were reported for the cathodic reaction, namely, hydrogen evolution/7/. The lower current efficiency for CO_2 evolution can be attributed to surface oxidation of coal as evidenced by a decrease in current with time. The oxidation rate was low (a few mA/cm^2) at cell potentials of ~0.8 V. It was suggested that a significant enhancement in rates would be possible by carrying out the reaction at 200-600°C.

Okada et al/44/ observed current densities of up to 100 A/m^2 for electrolytic hydrogen production, at a cell voltage of ~1.0 V, using an unwashed lignite coal slurry. Carbon/44/ and soft coals/2/ yield higher currents as compared to hard coals. Okada et al also showed that the current densities obtainable with a particular coal depend upon their iron content. Thus, the current densities fell by two orders of magnitude when the coal samples were washed free of iron. These results were also confirmed by other workers/45,46/. Senftle et al/47/ identified aromatic acids as byproducts during the oxidation of anthracite.

It appears that considerable improvements in coal slurry electrolysis must be accomplished, before acceptable current densities of 1000-5000 A/m^2 can be obtained.

Along with coal, crushed oil shale and peat could function as anode depolarizers in water electrolysis.

<u>SO_2 As The Anodic Depolarizer</u>

Electrooxidation of H_2SO_3 to H_2SO_4 is the electrochemical step in the Westinghouse thermochemical-electrochemical hydride

cycle/4/ for hydrogen production. The anodic and cathodic reactions involved are:

At anode $H_2SO_3 + H_2O \rightarrow H_2SO_4 + 2H^+ + 2\bar{e}$

At cathode $2H^+ + 2\bar{e} \rightarrow H_2$

Overall reaction $H_2SO_3 + H_2O \rightarrow H_2SO_4 + H_2$

The thermodynamic reversible potential for this reaction is only 0.17 V as compared to 1.23 V for water electrolysis.

Sulfuric acid, if produced in high enough concentrations, could be a useful product and the sulfur dioxide required for this reaction may be made available from stack gases.

An SO_2 depolarized cell operates at a potential about 0.8 V below that of the non-depolarized cell giving rise to energy savings. The sale of sulfuric acid should lead to further reductions in the cost of hydrogen.

The following two problems are encountered with the sulfurous acid oxidation reaction:

- Migration of H_2SO_3 to the cathode causes its reduction to sulfur which poisons the cathode. A suitable membrane, impermeable to this species is not available.

- Increase in acid concentration results in higher open circuit potentials. Thus the cell potential will be of the order of 0.8 - 1.0 V at practical current densities (~200 mA/cm^2). While this means a reduction in electric energy consumption of 40-60% compared with conventional or advanced water electrolyzers, the cost of sulfurous acid will have to be taken into account if it is not available at negligible costs.

10.0 CONCLUSIONS AND RECOMMENDATIONS

The increased use of electrolytic hydrogen in a Hydrogen Energy Economy will offer new opportunities for Ontario Hydro. In addition to load growth it offers the possibility for load levelling. Projection of the time at which such a positive effect will be felt is difficult but two things appear certain. First, hydrogen as an energy carrier offers the best hope, to date, for continuing current lifestyles in a world depleted of its traditional fossil resources. Second, a full fledged Hydrogen Energy Economy is unlikely during the next two decades. Further, major political or economic upheavals and

technological breakthroughs in hydrogen generation, storage and utilization can have a profound impact on the realization of a Hydrogen Energy Economy. Major research efforts are being made in different countries that may bring us closer to the increased use of electrolytic hydrogen. Locally, the Institute of Hydrogen Systems is conducting significant research that could benefit Ontario Hydro.

A major effort to conduct in-house research is perhaps not justified in the near future (5-10 years). A close monitoring of the technologies on a periodic basis is necessary to a) provide timely alert of any major advancements in electrolyzer and fuel cell technologies, and b) explore other non-utilization applications within Ontario Hydro.

It is recommended that OHRD:

i) conduct periodic reviews on water electrolyzer technologies preferably in collaboration with the Institute of Hydrogen Systems,

ii) explore non-utilization applications, such as tritium related applications, when warranted, and

iii) conduct prototype evaluations of advanced electrolyzers, eg vapour phase electrolyzer based upon proton conducting electrolytes, as they come closer to commercialization.

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